

The potential radionuclide migration role of bitumen colloids at SFR

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Contents

1	Background	5
2	Implications for SFR	9
2.1	Colloidal stability	9
2.2	Experimental evidence	10
2.3	Handling of bitumen colloids at the PSU	11
	References	13

1 Background

Bitumen as waste packaging material is a colloidal material in itself. Although bitumen presents a hydrophobic character, it can be dispersed in water. The colloidal structure of the bitumen matrix is mainly composed of asphaltenes; the core of the micelles, surrounded by resins and non-polar compounds. Saturated and non-polar compounds compose the dispersing phase. The asphaltenes and resins are bound by hydrogen bonding.

When bitumens are dispersed in water, most of these H-bonds are broken and they become ionisable. The sign of the surface charge then becomes pH-dependent.

The amphoteric behaviour of bitumen dispersions has been rationalised in terms of the predominance of carboxylic groups at low pH and amine-containing groups in alkaline media.

An Ionizable Surface Group model (ISG) can be used to approximate the Stern layer potential and consequently the colloidal stability as a function of pH (Stumm 1987). This can be experimentally established by the determination of the Zeta potential of the colloidal suspensions. Takamura and Chow (1985) adopted the ISG model in order to model the electric properties of the bitumen/water interface.

Experimental work on bitumen-water dispersions indicates that the presence of Na^+ increases the stability of the bitumen-water dispersions (Rodríguez-Valverde et al. 2003).

The bitumen-water dispersions were put in contact with solutions of varying Na^+ concentration as given in Table 1-1.

According to these investigations, the electrophoretic mobility increases with pH (Figure 1-1).

Table 1-1. Initial sodium concentration and average particle radii of bitumen-in-water dispersion.

Dispersion	$[\text{Na}^+]_0$ (mM)	\bar{a} (μm)
D1	100	0.63 ± 0.20
D2	9.4	0.63 ± 0.12
D3	1.0	0.93 ± 0.15
D4	0.1	2.00 ± 0.42

A log-normal distribution in size was assumed.

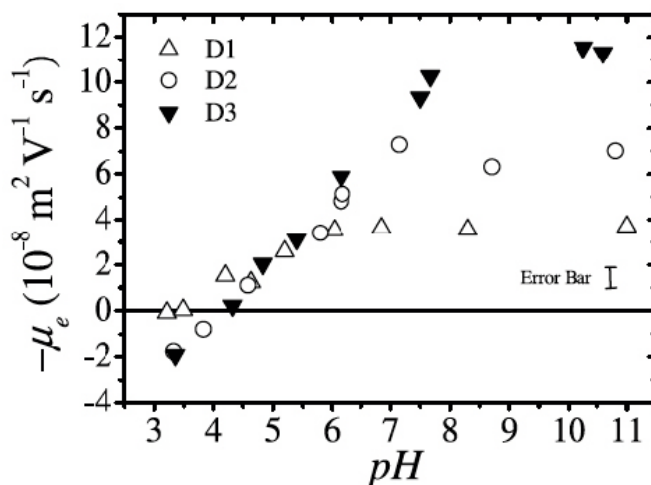


Figure 1-1. Electrophoretic mobility versus pH for dispersions D1, D2 and D3. The maximum experimental error in mobility is indicated. Notice the reduction of electrophoretic mobility at $\text{pH} > 6$ when the initial electrolyte concentration increases due to the screening effect of the thick double electric layer (from Rodríguez-Valverde et al. 2003).

As expected, the increased electrophoretic mobility with pH is a consequence of the increase of negative surface charge at alkaline pH values (Figure 1-2 and Figure 1-3). In these figures the reduced surface potential, expressed as the product of the surface potential times the electron charge divided by the Boltzmann constant and the temperature in kelvins, is plotted against pH.

In a cementitious environment, the presence of relatively high Ca^{2+} concentrations could decrease the zeta potential of the bitumen dispersions and consequently the electrophoretic mobility. The measurements up to 1 mM Ca^{2+} concentration support this hypothesis, to a certain extent, although, even at millimolar Ca^{2+} the measured Z-potential is still quite negative (Figure 1-4).

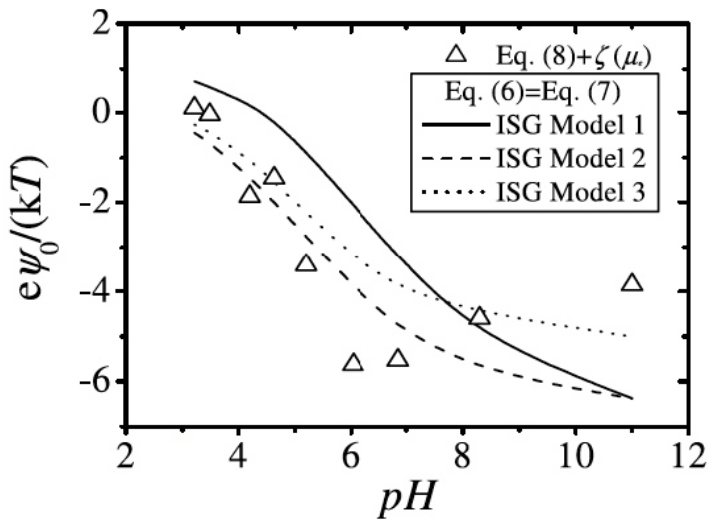


Figure 1-2. Reduced surface potential versus pH for dispersion D1 using two methods. The points are computed from the zeta potentials (eq.(8)) obtained by means of the electrophoretic measurements (Figure 1-4). The lines match the solution of the system formed by Eqs. (6) and (7) for the three ISG models summarized in Table 2-1 as described in Section 2.2 (from Rodríguez-Valverde et al. 2003).

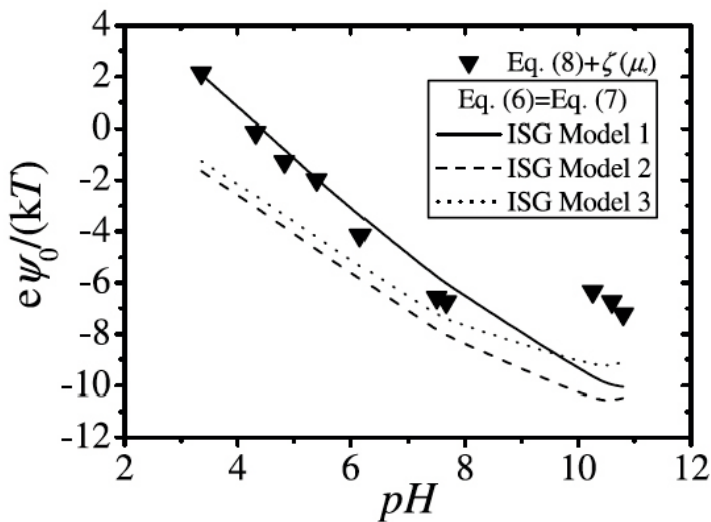


Figure 1-3. Reduced surface potential versus pH for dispersion D3. A patent discord is present at high pH just like happens for other dispersions. This disagreement illustrates an overestimation in the values of zeta potential used to compute the surface potentials (from Rodríguez-Valverde et al. 2003).

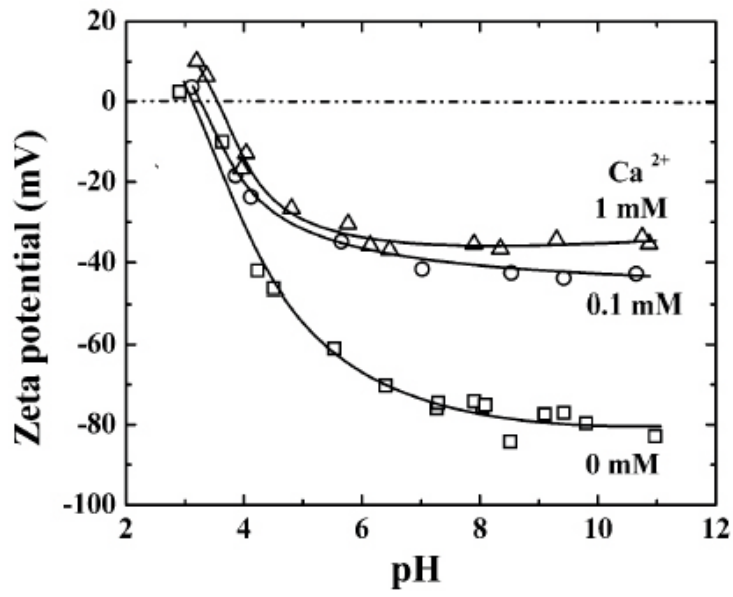


Figure 1-4. Zeta potential of the bitumen dispersions in the presence of calcium as a function of pH. (Liu et al. 2003).

2 Implications for SFR

2.1 Colloidal stability

It is clear that bitumen colloids are quite stable at alkaline pH values and that their stability is not much affected by the presence of Ca^{2+} concentrations in the millimolar range. Hence, cementitious environments are not a clear guarantee of bitumen colloidal destabilisation.

There two questions that still remain:

1. Which are the maximum concentrations of bitumen colloids to be expected at SFR?
2. How will bitumen colloids interact with the aqueous radionuclides?

There are no direct determinations of bitumen colloidal concentrations under these circumstances and, despite the presence of bitumen-conditioned waste in many repositories, most SA have tended to neglect bitumen colloids. Indeed, a recent review of near-field colloids by Swanton et al. (2010) noted the absence of experimental information specifically on bitumen colloids, but the current interest in shale oil and gas reservoir exploitation has triggered some research on the interaction of asphaltenes with geological materials.

Particularly interesting is the work of da Silva Ramos et al. (2001) who studied the adsorption of asphaltenes onto silica gel. The adsorption data are shown in the Figure 2-1.

The data indicate that equilibrium concentrations of asphaltene suspensions in the 0.1 g/L range can be achieved in equilibrium with sorbed/precipitated asphaltenes on silica gel.

Two combined waste equilibrium leach tests (ELTs), containing 17 different major ILW wastes expected to be present in the then-proposed Nirex repository have shown that a range of colloid types may arise from interactions of cement materials with waste components (Swanton and Vines 2003). Measured leachate colloid concentrations in supernatant leachates were low, about 10^{10} particles dm^{-3} , (100–5,000 nm size fraction) for supernatant leachates and less than 10^{11} particles dm^{-3} , (100–5,000 nm size) for drained leachates, in common with batch leaching experiments on cured NRVB (Swanton et al. 2010). Unfortunately, bitumen was not included in the waste matrices (Angus and Tyson 2002), so little can be drawn from these particular experiment.

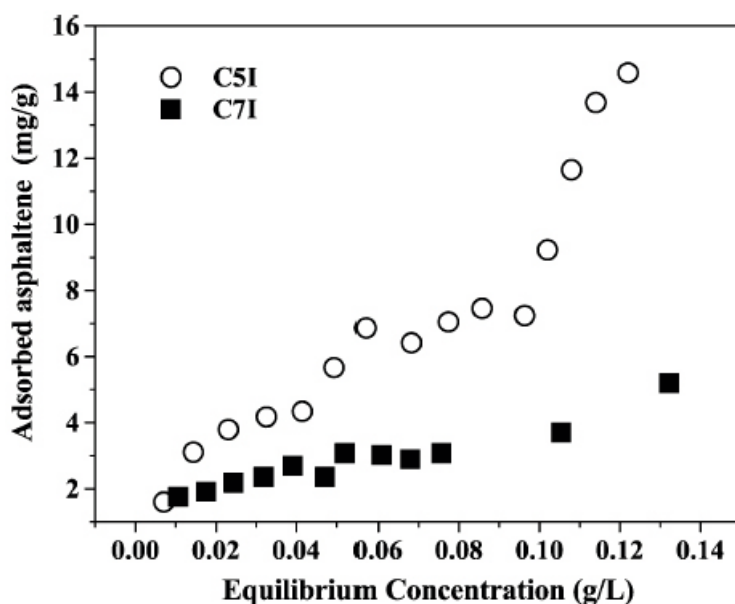


Figure 2-1. Adsorption isotherms obtained for C5I and C7I asphaltenes onto silica gel, at 25°C (from da Silva Ramos et al. 2001).

The next question to answer is, if bitumen colloidal suspensions are stable, could they mobilise radionuclides?

From the previous analysis it is clear that bitumen colloidal suspensions are stable at high pH due to their negative surface charge. Hence they will preferentially mobilise radionuclides that are positively or neutrally charged under SFR conditions.

By and large, there are two sets of conditions in SFR: most of the vaults are under cementitious conditions; this at high alkalinities and relatively high Ca concentrations, except for BLA where the bituminised waste is not surrounded by cement.

The aqueous speciation of the radionuclides Cs, Ni, Eu and Th under cementitious conditions in the SILO has been calculated in 3 scenarios (Table 2-1).

The results of the speciation are shown in Table 2-2.

2.2 Experimental evidence

Van Loon and Kopajtic (1991a, b, c) studied the sorption of Cs, Sr and Ni on bitumen. To this end, a bitumen suspension was prepared under highly alkaline conditions and equilibrated to the desired chemical conditions. The mechanisms of sorption could be identified and a sorption model for the 3 radionuclides was proposed. In the cases of Cs and Sr, ion exchange on the deprotonated carboxylic groups of the bitumen was the main sorption mechanism. It could be shown that, in the cases of Cs and Sr, competition mainly with Na, K and Ca present in the cement pore water resulted in very low sorption values on bitumen (Van Loon and Kopajtic 1991a). In the case of Ni, surface complexation is the dominating sorption process. For the latter radionuclide, competition with OH⁻ in solution caused a very low sorption value, because hydrolysed species were found not to sorb on the bitumen surface (Van Loon and Kopajtic 1991c). Model calculations made for U(VI) and Am(III) showed that also for these elements, only very low sorption values can be expected based on the formation of hydrolysed species in solution that – in analogy with Ni – are assumed not to sorb on bitumen (Van Loon and Kopajtic 1991c).

Table 2-1. Summary of the different scenarios considered. Green symbols indicate that the process has been considered; red symbols indicate that the process has been neglected.

Scenario	RN sorption	Organics sorption	RN complexation with organics
A	✓	✓	✓
B	✗	✗	✓
C	✓	✗	✗

Table 2-2. Summary of radionuclide aqueous speciation under SILO conditions.

Radionuclide	Scenario A	Scenario B	Scenario C
Cs	Cs ⁺	Cs ⁺	Cs ⁺
Ni	Ni(OH) ₃ ⁻ (or Ni(OH) _{2(aq)}) [*]	Ni(OH) ₃ (GLUH ₄) ²⁻ **	Ni(OH) ₃ ⁻ (or Ni(OH) _{2(aq)}) [*]
Eu	Eu(OH) _{3(aq)}	Eu(OH) ₃ (GLUH ₄) ⁻	Eu(OH) _{3(aq)}
Th	Th(OH) _{4(aq)} , Th(OH) ₄ (ISAH ₂) ⁻ and CaTh(OH) ₄ (ISAH ₂) _{2(aq)} ***	CaTh(OH) ₄ (GLUH ₄) _{2(aq)} ***	Th(OH) _{4(aq)}

* New thermodynamic data on nickel are available (Gamsjäger et al. 2005, Palmer and Gamsjäger 2010) and may indicate that Ni(OH)_{2(aq)} and not Ni(OH)₃⁻ could be the major species in solution in alkaline conditions.

**Data for nickel-GLU and nickel-ISA complexes in near-neutral to alkaline media are scarce. The re-evaluation of the available information conducted during the development of the “Simple Functions – Sorption” tool suggests that Ni-OH-GLU and Ni-OH-ISA complexes could be important under repository conditions. However, experimental data are necessary in order to confirm the exact formula and charge of the species formed.

***Available thermodynamic data for the formation of Ca-Th-OH-L (L=GLU, ISA) complexes indicate that these species may be relevant under the studied conditions. However, similar complexes have not been reported for nickel or europium, and the formation of those species should be considered with caution.

Consequently it may be concluded that, from a mechanistic point of view, bitumen colloids are likely to be stable and numerous, but are assumed to show no or only very weak interactions with radionuclides under the expected SFR conditions.

2.3 Handling of bitumen colloids at the PSU

From the previous mechanistic discussion, as well as experimental and natural systems evidences, we may conclude that bitumen colloids are likely to occur and they would be stable and numerous in cementitious environments. However, the extent of radionuclide complexation by bituminous colloids is expected to be low and therefore their potential contribution to radionuclide transport at SFR is deemed to be limited. Hence, no additional consideration at PSU radionuclide transport calculations appears to be appropriated in the light of the present evidences.

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