



Reactive behaviour of uranine (fluorescein) in a deep geothermal-reservoir tracer test

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A tracer test was performed in the geothermal research well Horstberg-Z1, located in the Northern German Basin. The test aimed to evaluate the fluid transport connection and the hydraulic properties of a hydrofrac created in about 3.8 km depth between two sandstone horizons separated by a layering of clay and sandstones. From an evaluation of massive hydraulic stimulation tests ('water-frac' technique) and hydraulic tests carried out earlier, it was suspected that the two sandstone horizons would be hydraulically connected by the artificially-induced large-scale fracture. Several thousand cubic metres of cold water were injected into the lower horizon, and tracer was added upon achieving unambiguous pressure response from the upper horizon. A tracer mixture consisting of uranine (disodium fluorescein), 1,5-naphthalene disulfonate (NDS) and tritiated water (HTO) was chosen with the aim of gaining additional information on fractured-porous structure characteristics, e.g. by virtue of the tracers' different diffusion coefficients, but also to check for possible anomalous behaviour of the organic tracers, with HTO serving as a reference. On-site, a flow-through filter fluorometer for uranine detection was installed in order to get immediate information on the tracer breakthrough curve (BTC) in the outflowing fluid, and samples were taken frequently for laboratory analysis of all tracers. However, no uranine signal was detected with the field fluorometer (neither before nor after pH adjustment).

The laboratory analyses comprised highly sensitive spectrofluorometry for uranine and NDS, and liquid scintillation counting for HTO, the latter possible only after distillation of the samples as these appeared as almost saturated NaCl brines with high content of dissolved Fe, Mn and other components not yet identified, the metals being

in solution by virtue of an extremely reduced character of the brine and a pH value around 5.5; in contact with air, excretion of green-brownish precipitates rapidly occurred. While NDS and HTO showed clear BTCs, uranine was found only in trace concentrations in a first series of spectrofluorometric analyses (with pH values accordingly adjusted). With progressing aeration, an increase of the uranine signals was registered. We explain this phenomenon by the reduction of uranine under the prevailing underground conditions (temperatures ranging between 130 °C and 140 °C, very low redox potential) to its non-fluorescent leuco-dye form, which in turn is sensitive to reoxidation. These reactions can be performed under adequate conditions in the laboratory and enjoy a variety of applications (e.g. in enzyme studies). However, to our knowledge, the uranine reduction to its leuco-dye form has not been documented during water tracing tests hitherto. The intricate brine behaviour (precipitation, influence of unidentified ingredients) did not allow exact quantitative determination of original uranine concentrations, but after partial reoxidation in the laboratory a plausible uranine BTC was obtained: tracer recoveries amounted to 6.4% (uranine), 7.4% (HTO), 10% (NDS), after an outflow volume of about 2.8 times the injected chaser volume; extrapolated to the time at which the free outflow rate would approach zero, tracer recovery levels would not exceed 13% for either tracer, and overall low recoveries were expected from the divergent flow-field geometry. It thus turns out that 'uranine disappearance' was not primarily by adsorption onto rock surfaces (the more so as sorption is generally expected to decrease with temperature), but by reactions taking place in the aqueous phase. The BTC difference between NDS and HTO could consistently be explained by their different diffusion coefficients. Two alternative models existed for the geometry and size distribution of the structures composing the hydrofrac [1, 2]; to aid finding out which of them more realistically describes flow and transport in the candidate geothermal reservoir, a BTC analysis instrument proposed by G. M. Shook [3] was applied to the NDS signal.

Uranine is most popular for its easy online detection, and online filter-fluorometer readings are often taken as a basis for deciding when to discontinue sampling; in the case study presented here, the absence of any uranine signal on-site had scarcely failed to lead to a wrong decision (under the impression that 'the whole tracer' would have flown to a different direction). Worth mentioning, also, even in deep crystalline rocks (with in-situ temperatures <120 °C, in tracer tests conducted in Germany at the pilot hole of the Deep Continental Drilling "KTB", 2003-2005), for which it had been regarded as conservative, uranine systematically showed slightly lower recoveries than NDS or HTO - which still awaits explanation. Relying on uranine as a 'reference tracer' should be considered with care.

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References:

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