

THERMAL DECAY OF SELECTED ORGANIC SUBSTANCES AS "SMART TRACERS" IN GEOHERMAL RESERVOIRS

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ABSTRACT

The aim of the laboratory experiments presented here is to find a set of thermosensitive tracers to identify thermal characteristics in deep geothermal reservoirs during the long-term operation of a power plant. In the near future several short-term push-pull experiments are planned at different test-sites in northern Europe. As a first step we focus on tracers which fulfill the requirements of a short tracer test in a comparatively low-temperature regime (100-130°C).

Based on the experiences in hydrolysis reaction kinetics the influences of structural characteristics on the reaction kinetics are studied on 42 phenol acetates in order to transfer these findings to esters based on naphthalene sulfonate structures as demonstrated geothermal tracers to use them as reaction products for thermosensitive tracers.

Moreover, the reaction kinetic of a 2-ethylbutylphenol sulfonic ester is investigated as a potential practical thermosensitive tracer.

1. INTRODUCTION

Chemically inert tracers have been established as a powerful technique for the characterization of geothermal reservoirs. They are used for flow-path tracking and to estimate fluid residence times (Rose et al. 2001, Sanjuan et al. 2006). For such tests the applied tracer is required to show a preferably conservative behavior in the reservoir. Therefore, it must be stable under the physico-chemical conditions present in reservoirs and sorption processes must be negligible.

The use of a conservative tracer simultaneously with a tracer interacting at reservoir conditions in a specific way may result in a dramatic increase in the amount of information that can be obtained from such an experiment. Such an approach has already been carried out using tracers with different diffusion

coefficients to quantify the specific heat-exchanging surface area in the reservoir (Ghergut et al. 2007). Another technique uses tracers which decay under specific temperatures in order to track thermal fronts in the reservoir and to calculate a thermal drawdown (Tester et al. 1986, Robinson and Birdsell 1987).

For the future short term single well push-pull experiments are planned at different test sites in northern Europe. The tests will repeatedly be conducted at several stages during operation of the power plant to identify changes in the reservoir properties/conditions. It is planned to apply thermosensitive substances along with conservative tracers to also investigate temperature changes in the reservoir during power plant operation.

Based on the positive results of naphthalene sulfonates as conservative tracers (Ghergut et al. 2007) and the hydrolysis reaction with well defined temperature sensitive reaction kinetics (Robinson 1987) we investigate the structural elements of different phenol acetates. Their different structural elements affect the hydrolysis reaction kinetics and the thermal behavior of respective esters derived from hydroxynaphthalene sulfonates (naphthol sulfonates) is predictable. In a second step a 2-ethylbutylphenol sulfonic ester was synthesized and influences of salinity and pH on its hydrolysis were explored.

2. ARRHENIUS PARAMETERS OF PHENOLIC ESTERS MEASURED BY HS-SPME-GC-MS

Esterification has been established as a powerful derivatization technique for the analysis of phenols in water by GC-MS. This derivatization reaction is especially attractive as it is compatible with solid phase microextraction (SPME) and thus the complete analysis can be fully automated (Buchholz 1994). Considering the large number of analytes, which are possible to detect simultaneously in one sample by this approach under controlled and identical conditions, this method is most suitable to investigate the influence of structural differences in phenolic

acetates on their hydrolysis kinetics. Data quality and comparability in the reaction constants between the investigated compounds has been shown to be very accurate (Bierwagen and Keller 2000). This is the only experimental design in which the sterical inhibiting influences of substituted groups can be investigated together with inductive and mesomeric effects of different substituents on the molecule with a high precision. Due to the highly ionic character of the sulfonic group, naphthol sulfonate esters cannot be studied by the same technique. Therefore, phenolic esters without sulfonic groups are analyzed instead in order to transfer the results of structural effects influencing the kinetics of hydrolysis to naphthol sulfonate esters.

2.1 Experimental method

The Arrhenius parameters for 42 phenolic esters as acetates were identified using a HP 6890 GC system with a HP 5972A mass selective detector from Hewlett Packard and a solid phase micro extracting (SPME) system from CTC Analytics.

For the sample preparation 150 mg NaHCO₃ were added to 1 ml of a 12.5 µg/l standard mix which included all 42 phenols. Then the phenols were esterified by adding 50 µl of acetic anhydride. The pH in this buffer system was 7.5 at room temperature. In order not to effect the measurements because of a beginning hydrolysis reaction the experiments were started directly after sample preparation.

For the experiments at ambient temperature a set of samples was prepared and then one sample was measured every 12 hours by headspace extraction on a Divinylbenzene/Carboxen/Polydimethylsiloxane 50/30 µm fiber with subsequent thermodesorption in the GC injector followed by GC-MS analysis. With this schedule at least 4 data points within 168 hours after sample preparation were obtained for the decrease in concentration in the consecutive determination of the hydrolysis constant k.

The measurements at elevated temperatures were carried-out by isothermally incubating the samples in the heater of the CTC auto-sampler feeding the GC-MS. In this experimental set-up only six samples could be heated simultaneously, therefore two schedules were chosen to cover at least 4 data points of every compound. The thermal decay constants of every compound were determined at 50, 60 and 70 °C.

The investigated character of ester hydrolysis reaction is given by Figure 1:

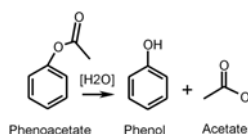
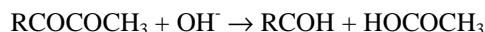


Figure 1: Hydrolysis reaction of phenol acetate

Regarding pH, the hydrolysis reaction is either acidic or alkaline controlled by different mechanisms. As most geothermal fluids are buffered naturally, the alkaline reaction mechanism will control its kinetics:



For this second order reaction the value of the kinetic constant k can be calculated by:

$$dC/dt = -k[\text{OH}^-] \cdot C \quad (1)$$

where t is the time, C is the concentration of the ester and k is the reaction kinetic constant

For nearly constant OH⁻ concentrations as existing in buffered systems the reaction can be assumed as pseudo-first order and k can be calculated by:

$$dC/dt = -kC \quad (2)$$

rewrite:

$$\ln\left(\frac{C}{C_0}\right) = -kt \quad (3)$$

with k being a function of pH.

The half-life times in (pseudo-) first order kinetics can be calculated by:

$$t_{1/2} = \frac{\ln 2}{k} \quad (4)$$

The temperature-dependence of k can be described by Arrhenius' law:

$$k = A e^{-E_a/RT} \quad (5)$$

where A is the pre-exponential factor, E_a is the activation energy, R is the ideal gas constant and T is the absolute temperature.

Together with the compound specific Arrhenius parameters and the decrease in concentration with time the specific temperature in the reservoir can be calculated from (4) and (5).

2.2 Results

a) Experiments at ambient temperature

By plotting the rate constants k for the hydrolysis reactions versus the pK_a of the non esterified substances it can easily be demonstrated that the

reaction rate increases by up to 4 orders of magnitude with increasing acidity of 3 orders of magnitude for the acid constant K_a . Furthermore this correlation is linear for at least 3 groups of substances (Figure 2). As expected, this proves that Hammett's law is valid for this type of reaction as well as substance class and thus transferable to other compounds. The classification into three groups agrees with the molecular structure of the compounds as each involves substances that have several similarities concerning their chemical structure. In one group a chlorine atom is located next to the hydroxyl group and in the second group two chlorine atoms are located next to the hydroxyl group. As a result the ester is better protected from hydrolysis attack by water molecules and the reaction rate decreases.

Also mesomeric (M) and inductive (I) effects from different substituents affect the hydrolysis reaction rate. If the substituents are not in a direct neighbor position to the hydroxyl group their sterical hindrance effect can be neglected and the effect on hydrolysis kinetics is solely assigned to the substituents' electron density influence on the aromatic ring(s). This effect can be studied best by comparing the reaction rates of respective phenolics (i.e. 3,5-DMP vs. 3,5-DCP) in table 1. Functional groups which possess a positive inductive effect (+I) lead to a decreased reaction rate (e.g. alkyl groups) and functional groups with a negative inductive effect (-I) increase reaction rates (e.g. Cl). By increasing the number of substituents this effect is intensified. Therefore, most of the trimethyl phenols are significantly more stable than cresols and the chloro phenols with a single chlorine group are more stable than their higher chlorinated analogues.

It must be concluded, that for substituents with a negative inductive effect (-I) the steric hindrance effect as a counter effect on the hydrolysis reaction rate is significant. For substituents with a positive inductive (+I) effect on the aromatic ring system the addition of steric hindrance can be neglected, as long as the alkyl groups are small (up to C3).

Following QSAR strategies (Hansch et al. 1995) these mechanisms controlling the hydrolysis kinetics may be transferred to esters of more complex phenolic compounds. This can be seen on the acetates of naphthol and 2-hydroxy biphenyl which plot on the same regression line as phenol acetate (Figure 2). As such, it can be predicted how the acetate esters of naphthol sulfonates would behave. First of all, the sulfonic group with its pronounced negative inductive effect (-I) combined with its negative mesomeric effect (-M) will decrease the electron density in the aromatic system and thus make the hydroxyl group more acidic and the respective esters less stable. This higher acidity of the hydroxyl group compared to naphthol is supported by the experimental data of Zollinger and Büchler (1950) who present lower pK_a values for sulfonated naphthols compared to naphthol. As a consequence, the hydroxyl group and the sulfonic group must not be on the same aromatic ring in order to keep the accelerating effect of the sulfonic group on the hydrolysis as low as possible. Furthermore, the number of sulfonic groups should be as low as possible. However, it should be at least one sulfonic group since the overall aqueous solubility is controlled by the sulfonic group.

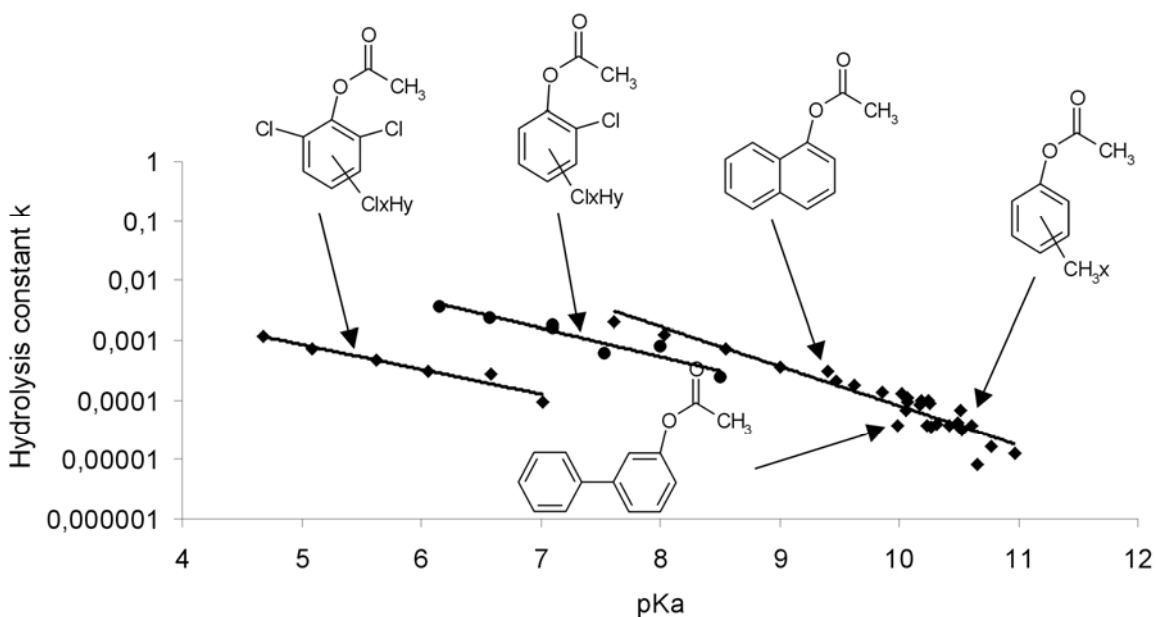


Figure 2: Hydrolysis constant k at ambient temperature versus pK_a

Table 1: Arrhenius parameters and calculated half-life times for 30°C and 110°C for 42 phenolic esters. Abbr.: DMP: Dimethyl phenol, TMP: Trimethyl phenol, EP: Ethyl phenol, PP: Propyl phenol, Kre: Cresol, CP: Chloro phenol, DCP: Dichloro phenol, TrCP: Trichloro phenol, TeCP: Tetrachloro phenol, PCP: Pentachloro phenol, pKa values were calculated using SciFinder ScholarTM

Substance	pKa	Ea [kJ/mol]	lnA [h ⁻¹]	A [h ⁻¹]	t 1/2 30°C [h] (calculated)	t 1/2 110°C [h] (calculated)	k at ambient temperature [L ⁻¹ mol ⁻¹ min ⁻¹]
PCP	4,68	61,93	22,28	4,74E+09	8,87	0,05	1,18E-03
2345TeCP	6,15	58,35	21,35	1,86E+09	5,37	0,04	3,74E-03
2,3,5,6 TeCP	5,09	72,20	25,87	1,72E+11	15,02	0,03	7,26E-04
2,3,4,6TeCP	5,63	80,54	28,75	3,06E+12	23,88	0,03	4,62E-04
3,4,5TrCP	7,61	71,07	25,85	1,68E+11	9,75	0,02	2,00E-03
2,4,5TrCP	7,1	71,79	26,11	2,19E+11	9,99	0,02	1,80E-03
2,3,4 TrCP	7,1	72,63	26,37	2,83E+11	10,83	0,02	1,63E-03
2,3,5TrCP	6,57	71,34	26,03	2,01E+11	9,08	0,02	
2,4,6TrCP	6,59	79,89	27,93	1,35E+12	41,74	0,05	2,74E-04
2,3,6TrCP	6,06	82,69	29,16	4,59E+12	37,61	0,04	2,99E-04
3,4DCP	8,55	81,53	29,39	5,77E+12	18,77	0,02	7,38E-04
2,4,2,5DCP	8	82,57	29,82	8,93E+12	18,41	0,02	8,06E-04
2,3DCP	7,53	87,13	31,43	4,47E+13	22,88	0,01	6,30E-04
2,6DCP	7,02	95,66	33,29	2,86E+14	109,53	0,03	9,47E-05
3CP	9	88,50	31,37	4,20E+13	42,23	0,02	3,64E-04
4CP	9,47	89,26	31,56	5,05E+13	47,69	0,03	2,12E-04
2CP	8,5	93,32	33,02	2,18E+14	56,35	0,02	2,43E-04
3,4,5TMP	10,5	93,31	31,81	6,53E+13	186,99	0,07	6,56E-05
2,3,5TMP	10,5	87,38	28,75	3,06E+12	369,76	0,23	3,09E-05
2,3,6TMP	10,8	65,55	19,38	2,60E+08	690,17	2,73	1,69E-05
2,4,6TMP	11	77,46	24,25	3,41E+10	621,35	0,90	1,24E-05
3,5DMP	10,2	91,19	31,26	3,75E+13	139,36	0,06	8,47E-05
3,4DMP	10,2	92,31	31,70	5,81E+13	140,57	0,06	3,69E-05
2,5DMP	10,4	85,58	28,08	1,56E+12	353,47	0,26	3,74E-05
2,4DMP	10,6	87,58	28,92	3,61E+12	340,08	0,21	3,70E-05
2,6DMP	10,7	72,35	21,79	2,91E+09	937,67	2,09	8,10E-06
3nPP	10,1	91,51	31,15	3,38E+13	175,51	0,08	9,45E-05
3iPP	10	85,22	28,88	3,49E+12	136,81	0,10	1,31E-04
4iPP	10,2	89,77	30,44	1,66E+13	178,03	0,09	9,83E-05
2iPP	10,5	79,39	25,58	1,28E+11	358,64	0,44	4,07E-05
2nPP	10,5	81,46	26,43	3,00E+11	351,56	0,36	3,65E-05
3EP	10,1	86,27	28,77	3,12E+12	233,26	0,08	6,75E-05
4EP	10,3	86,85	29,70	7,92E+12	115,81	0,08	9,86E-05
2EP	10,3	81,69	26,43	3,02E+11	383,77	0,39	3,45E-05
m-Kre	10,1	96,95	33,46	3,39E+14	154,75	0,04	1,07E-04
p-Kre	10,3	99,63	34,47	9,35E+14	164,60	0,04	8,91E-05
o-Kre	10,3	91,78	30,70	2,15E+13	307,45	0,13	3,86E-05
4Cl-3-Kre	9,63	91,06	31,74	6,06E+13	81,76	0,04	1,77E-04
2PhenylP	9,99	100,01	33,83	4,91E+14	363,75	0,08	3,64E-05
Phenol	9,86	96,38	33,55	3,69E+14	113,20	0,03	1,39E-04
Naphthol	9,4	53,92	17,50	3,99E+07	42,43	0,45	2,98E-04

b) Experiments at elevated temperatures

By plotting the half-life times calculated from the Arrhenius parameters versus the pKa it can be seen that the results from structural influence effects listed in 2.2.a could be confirmed (Figure 3). The half-life times decrease on average by three to four orders of magnitude with increasing temperature from 30 to 110°C. Depending on Ea and A the decrease in half-life times with increasing temperatures differs between the esters. An example of some selected substances is given in Figure 4.

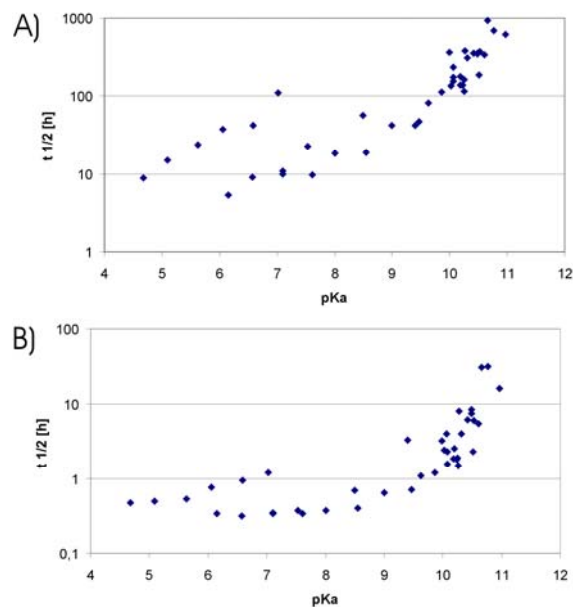


Figure 3: Calculated half-life times from Arrhenius parameters for 30°C (A) and 70°C (B)

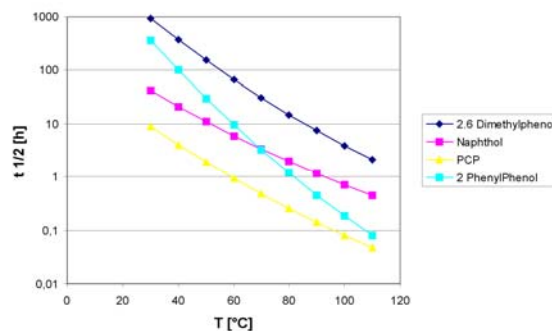


Figure 4: Calculated half life times versus temperature for 2,6 Dimethyl phenol, Naphthol, Pentachloro phenol and 2 Phenyl Phenol

3. HYDROLYSIS KINETICS OF NAPHTHOL SULFONATE ESTERS

Different isomers of naphthalene sulfonates have been successfully used as conservative tracers in geothermal reservoir investigations (Rose et al. 2001, Sanjuan et al. 2006, Ghergut et al. 2007). They are non-toxic, have a low detection limit by fluorescence and due to their highly ionic character they are highly soluble in water and show nearly no interaction with the solid phase. Based on these characteristics we chose this class of substances as base molecules. The thermosensitive character is introduced in these molecules by esterification of the hydroxyl group in naphthol sulfonates. As the sulfonic group is not altered a high solubility is maintained.

3.1 Experimental method

The esters based on 2-hydroxy-6-naphthalene sulfonate were selected to be most suitable, as the respective hydrolysis product 2-hydroxy-6-naphthalene sulfonate shows a high fluorescent signal at 230/430 ex/em. The esters themselves are not fluorescent. The limit of detection is 5 µg/l with direct fluorescence and <1µg/l with high pressure liquid chromatography using fluorescence detection.

The investigated character of ester hydrolysis reaction is given by Figure 5:

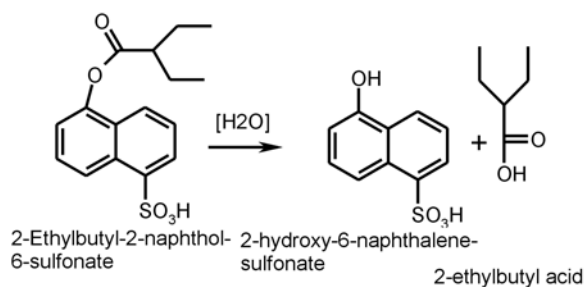


Figure 5: Hydrolysis reaction of 2-Ethylbutyl-2-naphthol-6-sulfonate

The naphthol sulfonic ester was synthesized by heating equimolar ratios of hydroxynaphthalene sulfonic acid with the organic acid chloride in dry dimethyl formamide under reflux for 10 hours. The purification was carried out by column chromatography and recrystallization techniques. LC/MS measurements confirmed a purity >95%.

The method of initial concentration was applied to identify the kinetic parameters. All chemicals used were of the highest available purity and the water was ultra-pure. For each measurement, four samples with different initial ester concentrations were prepared by adding a subsequent volume of ester standard to 4 ml buffer solution containing 2 g/l phosphate buffer in 5 ml glass vials for every investigated pH. The vials were incubated in a gas chromatographic oven at the temperature of investigation. After sufficient hydrolysis time (one half-life time) the concentration of resulting naphthol sulfonate was determined immediately using an Eclipse Cary 50 fluorescence spectrometer from Varian.

The respective pOH/pH concentration of the applied phosphate buffer at elevated temperatures was calculated using PHREEQC.

3.2 Results

The experiments show that the reaction kinetics of the hydrolysis reaction depends strongly on pH of the solution. The half-life times decrease by a factor of approximately 20 from pH 4.8 to 7.8 (Figure 6).

First experiments with brines containing 100 g/l NaCl show that there is no significant influence on reaction kinetics. The addition of powdered sandstone material acting as possible reacting surfaces demonstrated to have no significant effect either.

Considering the typically low acidity in European geothermal reservoirs with pH ranging from 5.0 to 6.0 (Wolfgramm 2008) due to high CO₂ reservoir concentrations and moderate temperatures of 100 to 130 °C, the reaction rates of the 2-ethylbutyl naphthol sulfonic ester may already be too fast to be used as a practical tracer for geothermal push-pull tests. It may however already be practical for the lower temperatures encountered in the injection well of a doublet.

There are now several possibilities to reduce the reaction rates of hydrolysis by modifying the base molecule. The first option is to use the results presented in chapter 2.2 by adding groups to the molecule which cause sterical hindrance and/or have positive inductive (+I) effects. Another possibility is to esterify the hydroxyl group of the base molecule with acids other than 2-ethylbutyric acid. It is known that acids with longer or multi-branched alkyl chains can result in a sterical hindrance to the ester group leading to slower reaction rates (Organikum 2004).

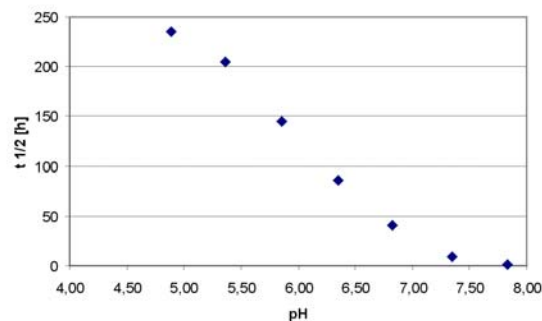


Figure 6: Half-life times of 2-Ethylbutyl-2-naphthol-6-sulfonate for different pH at 90°C

4 CONCLUSIONS

The hydrolysis of organic esters is regarded as an appropriate reaction with sensitivity to the thermal variability observed in geothermal reservoirs. The strong influence of the reaction product acidity on the reaction kinetics allows covering a broad range of different temperatures in the reservoir and different tracer test times. The linear relationship in this

context allows the prediction of reaction rates if the hydrolysis constants of similar substances are known. Furthermore, it is possible to control the kinetics of this reaction by the influence of the substituent's steric, inductive and mesomeric effects.

Therefore, the hydrolysis kinetics of selected naphthol sulfonic esters with varying pKa of the hydroxyl group and different chain length of the ester group are still under investigation. First results show a strong sensitivity on pH conditions in the reservoir. However, considering the naturally highly buffering character of geothermal brines it seems that these influences are predictable and can therefore be corrected.

Considering the presented experiments and the positive results from several tracer tests in the past, different isomers of naphthol sulfonate esters promise to be practical thermosensitive tracers in the characterization of low temperature deep geothermal reservoirs by short-term push-pull experiments.

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