

# Experimental Investigations of Hydrocarbon Fluid Recovery from Hydrothermally Treated Rocks of the Bazhenov Formation

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**Abstract**—The results of experimental shale-oil recovery from hydrothermally treated rocks of the Bazhenov Formation are discussed. It is shown that the yield depends on the duration of an experiment: the longer the hydrothermal impact is, the higher the oil yield is. The potential of oil recovery from hydrothermally treated rocks of the Bazhenov Formation is as high as 25 mg/g or 2.5 wt %. The addition of reducing agents such as aluminum or oxalic acid provides no increase in the coefficient of oil recovery. It is established that the yield of the oil fraction at 250°C is insignificant; at 300°C, it amounts to 25 mg/g, while at 350°C, it decreases up to 15 mg/g. This means that a temperature of 300°C is preferable, since it provides a higher yield of oil products and oil fractions are largely represented by normal alkanes, while chromatograms that were obtained at 350°C indicate the development of complex processes, including graphitization of kerogen.

**Keywords:** Bazhenov Formation, shale oil, oil recovery, hydrothermal treatment

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## INTRODUCTION

During recent years, technologies for shale-oil production have mostly been developed in the United States. The recent publications include many works that were dedicated to the recovery of fixed oil from different rocks and transformation of kerogen under the influence of different physicochemical factors. Moreover, their authors mostly investigated the transformation of organic matter in rocks in response to pyrolysis and the impacts of different chemical agents.

The previous investigations were usually aimed at revealing regularities in kerogen transformation in natural environments in order to understand the formation mechanisms of oil and gas accumulations (Ishiwatary and Fukushima, 1979; Burnham and Happe, 1984, Behar et al., 1992). Two aspects of experimental investigations may be defined: (1) pyrolysis in open and closed systems under low pressure or gas pressure and (2) hydrothermal transformation of organic matter in the presence of water. In recent years, some authors have assessed the petroleum-bearing potential of different rocks and changes of this potential under thermal impact for industrial hydrocarbon recovery (Behar et al., 2010; Pan et al., 2010; Rushdi and Simoneit, 2011; Zhang et al., 2014; Liang et al., 2015). At the same time, insufficient attention has been paid in these works to technologies for the extraction of shale oil and gas.

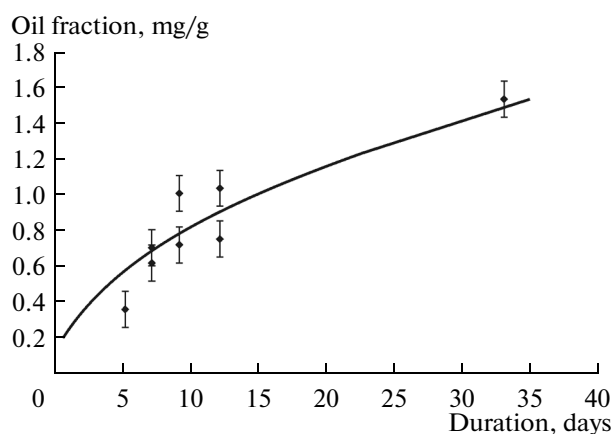
As a whole, both these aspects have similar patterns. For example, it has been established that kerogen that is heated to 250–300°C releases liquid and gaseous hydrocarbons. Moreover, the share of liquid

and gaseous (particularly, methane) fractions increases at low and high (over 400°C) temperatures, respectively. It has been shown that high hydrogen pressure is responsible for the reduced share of aromatic compounds and, correspondingly, an elevated yield of liquid products. It has also been revealed that the formation of hydrocarbons depends on the degree of primary organic-matter transformation and is most intense for kerogen of type I.

It has been established that the rate of the process and total hydrocarbon quantity are similar for hydrous and dry pyrolysis in closed systems, while in open systems, the rate of hydrocarbon generation is substantially lower. This is consistent with the kinetic model, according to which products of kerogen decomposition positively influence the formation of oil fractions and hydrogen that is released during the pyrolysis of aromatic compounds.

The share of organic carbon ( $C_{org}$ ) that is transformed into hydrocarbon fractions may be as high as 10%. Moreover, different rock samples display a large scatter of values. The maximum yield of hydrocarbons was obtained by researchers for samples from the Green River Formation (Uinta basin, United States). Behar et al. (2010) obtained a hydrocarbon yield of 620 mg/g, of which 420 and 200 mg/g are oil products and bitumen, respectively. Such values are characteristic of industrial objects that now provide production of shale oil.

In Russia, experimental investigations that are aimed at assessing the potential recovery of shale oil and gas from different rocks are scarce. The Bazhenov



**Fig. 1.** The correlation between the recovery of oil fractions from rocks of the Bazhenov Formation and experiment duration.

Formation is considered as one of the largest promising objects, but the potential of its rocks with respect to hydrocarbon extraction remains unclear. The discovered oil fields (Priobskoe, Prirazlomnoe, Pravdinskoe, Malobalykskoe, and others) that are confined to this unit stimulated the investigation of the geochemical and petrophysical properties of its rocks. The investigations included the analysis of the structure of the Bazhenov and uppermost Abalak formations as promising with respect to oil production (Balushkina et al., 2013; Kim and Rodchenko, 2013) and their reservoir properties (Khamidullin et al., 2013; Balushkina et al., 2014).

The purpose of this work was the assessment of the oil-generating potential of hydrothermally treated rocks of the Bazhenov Formation for hydrocarbon recovery.

## RESULTS AND DISCUSSION

The methods that were developed in the Laboratory of experimental geochemistry (Department of Geology, Moscow State University) for the study of mineral equilibria in hydrothermal environments were applied in these investigations. The experiments were conducted in heat-resistant steel autoclaves with a capacity of 50 l that were sealed with a copper gasket. Such autoclaves are able to maintain a temperature up to 600°C and pressure up to 20 mPa for a long period.

A 10 g rock sample that was taken from the Bazhenov Formation was placed in the autoclave. The sample was preliminarily crushed up to the fraction that is greater than 2 mm. The weight was augmented with a water solution so that the pressure at the temperature below the critical water point would correspond to that of the water vapor and at temperature above the critical value be as high as 100 mPa. The autoclaves were closed and then were placed in a preliminarily heated tubular furnace. The temperature

was set with an accuracy of  $\pm 3^\circ\text{C}$  using an OVEN TRM-10 PID controller and a chromel–alumel thermocouple. The duration of the heating (7 days) was determined using a kinetic series.

When the heating was complete, the autoclaves were cooled with running water and the gaseous phase was sampled. At a temperature of 200–350°C, the solution surface in the autoclave was covered with a hydrocarbon film. It was extracted using 5- or 10-ml of n-hexane and then its water and organic phases were separated in a separating funnel. After steaming of the solution of hydrocarbons in hexane, the quantity of oil fractions was determined by the weight method. Normal and isoprenide  $\text{C}_{10}\text{--}\text{C}_{35}$  alkanes, which are present in bitumoids and oils, were analyzed by the method of gas–liquid or gas chromatography using a Clarus chromatograph (Perkin Elmer Company). The parameters of the gas chromatographic analysis were as follows: the gas carrier was helium; the helium flow velocity was 30 cm/s at 100°C; the capillary quartz column was 60 m  $\times$  0.25 mm; the velocity of temperature programming in the column thermostat was 4°C/min; the initial and final temperatures were 60°C and 320°C, respectively. The solid phase of the samples was analyzed using a Rock-Eval-6 pyrolysis analyzer.

The kinetic series consisted of successive retrieval of similarly equipped autoclaves in a certain period. Sample 5209/126 was analyzed at a temperature of 300°C. The results of the analysis revealed that the longer duration of the experiment increased the recovery of oil fractions as determined by the hexane extract (Fig. 1). As a whole, the hydrocarbon concentration followed the equation

$$C = 0.258 \sqrt{t},$$

where  $C$  is the concentration of oil fractions (mg/g) and  $\sqrt{t}$  is time (days).

This equation was obtained with allowance for the assumed diffusion control of the hydrocarbon extraction from the analyzed rock, which corresponds to parameters of the rock–water interaction in the hydrothermal process. It appears that the same process also controls the recovery of physically fixed oil. It is conceivable that the initial stage of the process includes a latent period, which may be explained by both the dissolution of rock minerals and oxidation of hydrocarbons by residual oxygen that was captured during autoclave filling.

The quantity of oil fractions that were released from sample 5209/126 reached maximum values of 1.6 mg/g in 33 days. This value is substantially lower as compared with quantities that were obtained in similar experiments for rocks from the Green River Formation, which yielded values of 180 and even 400 mg/g (Behar et al., 2010). These low values for sample 5209/126 are explained by the high degree of kerogen transformation, which is established by the thermo-

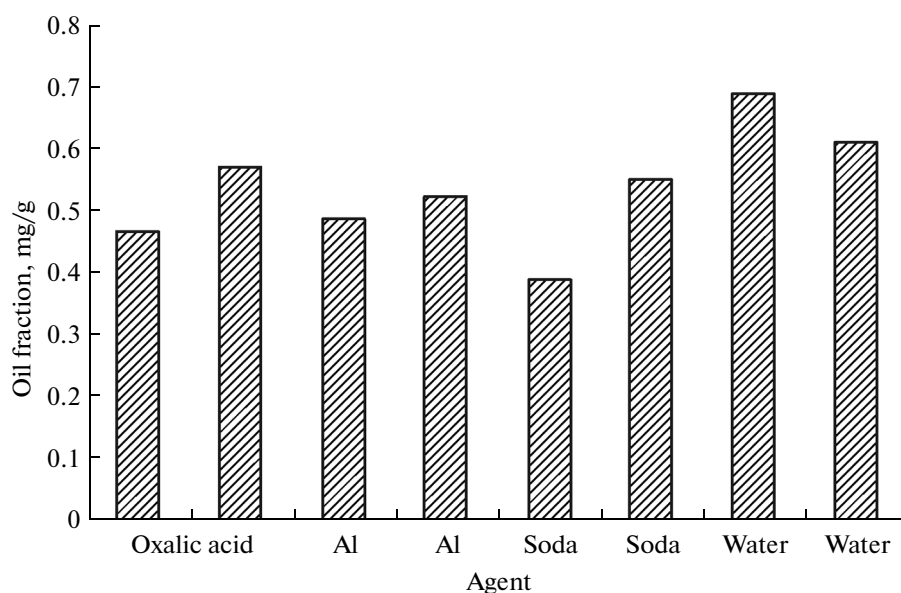


Fig. 2. The recovery of oil fractions from rocks of the Bazhenov Formation with the addition of different agents.

gravimetric analysis for samples from this part of the section. At the same time, the kinetic equation shows that rocks that are similar to sample 5209/126 may yield up to 19 mg/g of kerogen at 300°C under a 1 year impact. The kinetics of kerogen recovery requires additional investigation and study of all the products that were obtained in the experiments.

The sum content of  $C_{org}$  in sample 5209/126 was 11.33% and concentrations of S1 and S2 fractions were 7.93 and 65.35 mg/g, respectively. The maximum recovery with the Rock-Eval technique was observed at 434°C. The experimental data demonstrate that oil fractions that are fixed in kerogen are extracted only partly under hydrothermal impact. It is conceivable that accounting for gaseous and volatile fractions (some of which are lost during the processing of experiment products) will increase the share of extracted organic carbon.

For verification of the influence of chemical factors on the recovery of oil fractions, we conducted experiments with a variable composition of the solution. As some publications have shown that the recovery of oil fractions from kerogen increases in the presence of reducing agents, we performed experiments using oxalic acid and aluminum. Interaction of the latter with water at an elevated temperature results in the release of gaseous hydrogen and the formation of Al hydroxides (böhmite and diaspore) that are poorly soluble in water. In our experiments, the weight of the aluminum provided a partial hydrogen pressure of approximately 1.5 mPa. When heated, oxalic acid is decomposed in a complex process to form end products, viz., CO and CO<sub>2</sub>. The unsealing of autoclaves with added aluminum and oxalic acid was accompa-

nied by intense gas release, which indicates the development of the above-mentioned processes.

For destroying and dissolving the silica of the rock matrix, we used an sodium carbonate solution at a concentration of 0.05 mol/l. Such a solution is characterized by an alkaline reaction, which increases silica solubility. It was assumed that this solution accelerates the recovery of oil fractions.

This process was conducted at a temperature of 300 C during 7 days. Figure 2 and Table 1 present the results of these experiments, which are compared with the data that were obtained from the kinetic series that were conducted in pure water at the same temperature during 7 days as well. The quantity of extracted oil fractions appeared to be similar in these experiments, which may indicate the lack of any influence of reducing agents on the intensity of kerogen recovery.

To assess the influence of the  $C_{org}$  concentration in the rock on the recovery of oil fractions, the samples were selectively taken from a well 6452 section with

Table 1. Oil fractions of hydrocarbons recovered from rocks of the Baszhenov Formation with the addition of different agents

Agent	Agent quantity, mg/g	Recovery of oil fractions, mg/g
Oxalic acid	34	0.47
	168	0.57
Metallic aluminum	34	0.502
	35	0.532
Sodium carbonate	11	0.39
	11	0.55

**Table 2.** Geochemical properties of the organic component in samples taken for Rock-Eval experiments

Parameter	Sample number/depth, m			
	6452-22-m 2998.32	6452-41-m-1 2982.25	6452-61-m 2975.74	6452-80-m-1 2966.71
Qty, mg	40.75	21.36	29.37	29.43
$S_1$ , mg/g	0.48	1.43	7.61	7.55
$S_2$ , mg/g	4.66	5.61	57.1	78.53
PI	0.09	0.2	0.12	0.09
$T_{max}$ , °C	438	437	444	440
$S_3$ , mg/g	0	0	0	0
PC, %	0.44	0.6	5.39	7.17
RC, %	1.92	2.66	28.18	8.35
TOC, %	2.36	3.26	33.57	15.52
HI	197	172	170	506
pyroMINC, %	0.73	0.13	0.06	0.16
oxiMINC, %	0.02	0.14	0.48	0.12
MINC, %	0.75	0.27	0.54	0.28

(S1) free hydrocarbons, up to 300°C, mg HC/g of rock; (S2) hydrocarbon products of pyrolysis of kerogen and tar–asphaltene compounds, 300–650°C, mg HC/g of rock; (I) productivity index,  $S_1/(S_1 + S_2)$ ; ( $T_{max}$ ) temperature of maximal yield of hydrocarbons during kerogen pyrolysis, °C; (PC) organic carbon subjected to pyrolysis, wt %; (RC) residual (resistant to pyrolysis) organic carbon, wt %; (TOC) total  $C_{org}$  content in rocks, wt %; (HI) hydrogen index, mg HC/g  $C_{org}$ ; (OI) oxygen index, mg  $CO_2/g C_{org}$ ; ( $C_{min}$ ) concentration of mineral carbon in rock, wt %.

**Table 3.** Results of experiments on the recovery of oil fractions from rocks of the Bazhenov Formation, mg/g

Experiment, °C	Sample			
	6452-22-m	6452-41-m-1	6452-61-m	6452-80-m-1
250°	<0.1	<0.1	<0.1	<0.1
300°	1.3	1.8	24.4	8.0
350°	0.5	0.9	6.5	14.4

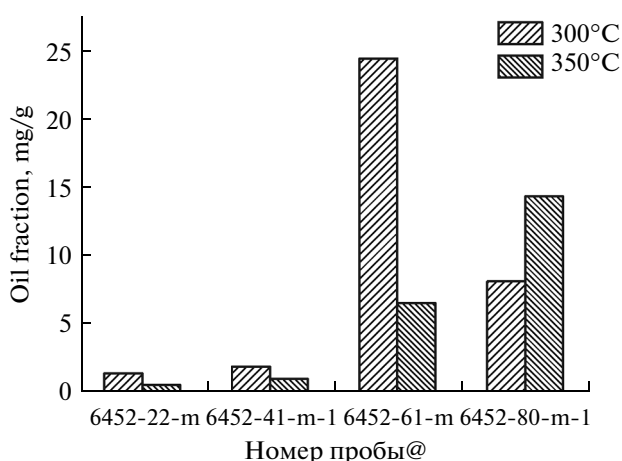
variable organic carbon contents. Table 2 presents the main parameters of the chemical composition of organic components from these samples. The content of total  $C_{org}$  is highly variable, ranging from 2.36 to

33.57%. The share of hydrocarbons that belong to the S1 and S2 groups is also variable.

The influence of temperature on the recovery of oil fractions was determined in experiments with samples at temperatures of 250, 300, and 350°C and the pressure of the saturated water vapor, as well as at a temperature of 470°C and a pressure of 100 mPa. The experiment lasted 7 days for all the temperature values.

No oil fractions were established in the experiments that were conducted at 470°C. The experiments were accompanied by the release of gases, which were not sampled, however, due to equipment issues. Such a result corresponds to the stage of high-temperature gas formation and cannot be investigated by these methods. The content of total organic carbon in rocks varied insignificantly. This is explained by partial dissolution of the mineral rock matrix simultaneously with gas release. The kerogen was most likely substantially graphitized. Thus, it may be concluded that high temperature is unfavorable for the recovery of oil fractions from rocks of the Bazhenov Formation.

Figure 3 and Table 3 illustrate the results of experiments at temperatures of 250, 300, and 350°C and the

**Fig. 3.** The results of experiments on recovery of oil fractions from rocks of the Bazhenov Formation.

pressure of the saturated water vapor (two-phase system). The yield of oil fractions at 260°C was low, never reaching 0.1 mg/g in all the samples. At 300 and 350°C, the recovery of the oil fractions varied from 1.3 to 24.4 and from 0.5 to 14.4 mg/g, respectively. It is noteworthy that a temperature increase from 300 to 350°C resulted in no increase in oil recovery. As the formation temperature in the examined section is as high as 80–100°C, reactions that stimulate the recovery of oil fractions may be activated by relatively insignificant heating.

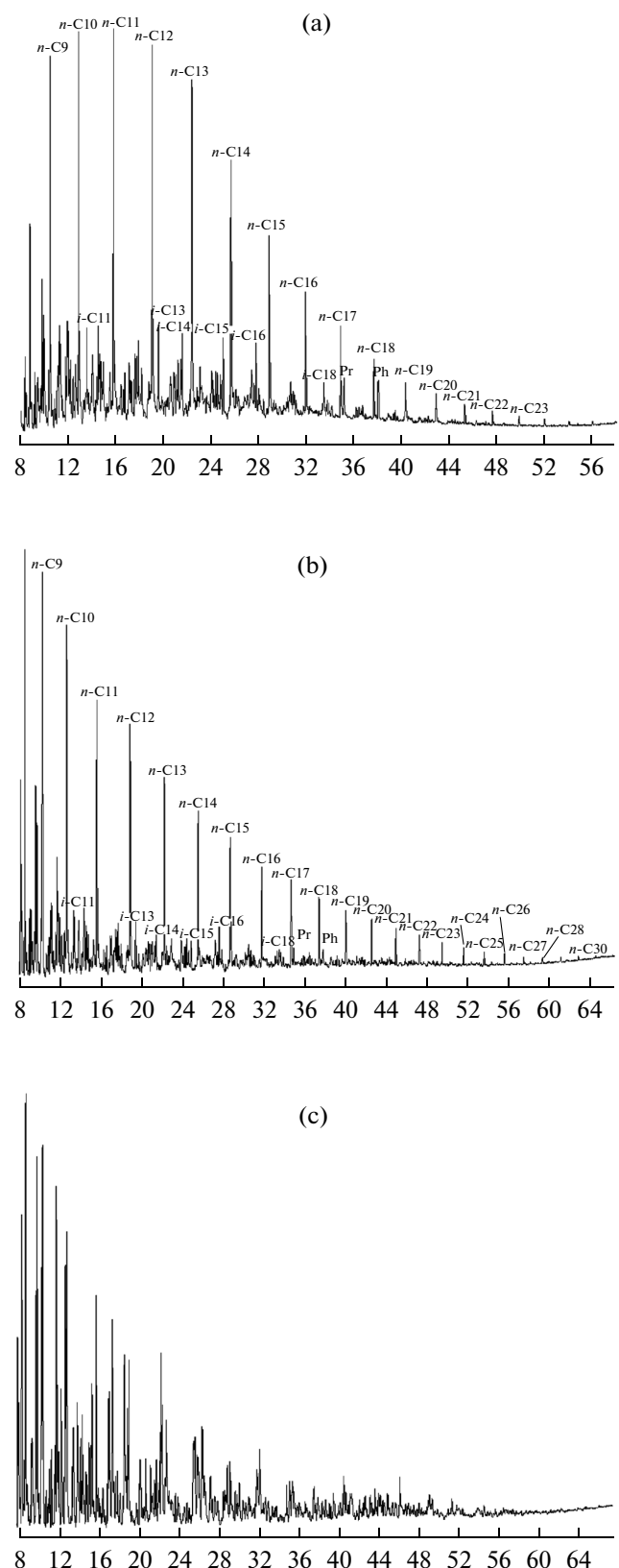
Chromatographic analysis was used to determine the composition of the oil fractions. Figure 4 illustrates the analytical data on oil fractions at temperatures of 250, 300, and 350°C. Table 4 presents data on the concentrations of normal alkanes and isoprenanes in oil fractions as determined by the method of liquid chromatography. It was established that the profile of the quantitative content of carbons with the chain length from C<sub>9</sub> to C<sub>30</sub> at a temperature of 250°C crosses the maximum. The systems are dominated by C<sub>10</sub>–C<sub>12</sub> hydrocarbons (Fig. 4a). The increase of temperature from 250°C to 300°C changes the quantitative proportions of the hydrocarbons: the maximum shifts to the left and systems become dominated by hydrocarbons with the chain length of C<sub>9</sub>–C<sub>13</sub>, with the maximum at C<sub>9</sub> constituting approximately 13% of the total hydrocarbon content (Figs. 4, 6).

It should be also noted that the increase of temperature from 250 to 300°C results in an increase of the contents of normal alkanes and a decrease in the quantity of isoprenanes in all the samples. These data indicate that the temperature increase stimulates the transformation of a progressively growing quantity of the organic component into normal alkanes and the length of the hydrocarbon chain decreases. It is conceivable that a further temperature increase should result in a reduced share of the oil fraction and recovery of a higher share of gaseous products with a chain length that does not exceed C<sub>5</sub>.

The chromatograms that were obtained for samples at temperature of 350°C are impossible to interpret (Fig. 4a), which is most likely because a mixture of many different organic products occurs. It is also conceivable that high temperatures trigger carbonification, which produces a complex mixture of different compounds. For example, it is known that such a temperature stimulates the formation of different aromatic compounds and asphaltenes.

## CONCLUSIONS

(1) The potential for the recovery of oil fractions from the hydrothermally treated rocks of the Bazhenov Formation amounted to 25 mg/g or 2.5 wt % in 7 days, which allows it to be evaluated as promising. Additional investigations are needed to reveal the correlation between the recovery potential and the geochemical properties of rocks. The assessment of the ratios



**Fig. 4.** The results of the chromatographic analysis of oil fractions from sample 6452-80-m-1 section that were recovered at temperatures of 250 (a), 300 (b), and 350°C (c).

**Table 4.** Results of the chromatographic analysis of oil fractions from rocks of the Bazhenov Formation that were recovered at temperatures of 250 and 300°C

Content, %	Sample							
	6452-22-m		6452-41-m-1		6452-61-m		6452-80-m-1	
	250°C	300°C	250°C	300°C	250°C	300°C	250°C	300°C
<i>n</i> -alkanes	88.5	91.5	87.8	91.3	79.7	89.0	84.5	89.9
isoprenanes	11.5	8.5	12.2	8.7	20.3	11.0	15.5	10.1

between the released oil, volatile, and gaseous fractions, which may enhance the sum potential of hydrocarbon recovery, requires of special equipment.

(2) Experimental investigations revealed that the maximum share of oil fractions that are extracted during the same period was formed at a temperature of 300°C. A temperature increase stimulated the release of the gaseous fraction and its decrease resulted in reduced recovery of hydrocarbons.

(3) Special experiments to study the kinetics of hydrocarbon recovery in closed and open systems and analysis of their products are needed to obtain kinetic equations and predict the behavior of the system in time. In addition, only such an approach would make it possible to establish the proportions between the recovered physically fixed and synthetic oil.

#### ACKNOWLEDGMENTS

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SPELL: 1. asphaltenes