THERMODYNAMIC PROPERTIES OF THE PALCHIG-OBA AND MUKHTADIR GEOTHERMAL RESOURCES OF AZERBAIJAN

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Measurements of (p,ρ,T) properties of Palchig-oba and Mukhtadir geothermal resources of Azerbaijan at T=(278.15 to 373.15) K and pressures up to p=40 MPa are reported. An empirical correlation for the density of the geothermal resources as a function of pressure and temperature has been developed. This equation is used to calculate other volumetric properties.

Geothermal energy is the heat from the Earth. It's clean and sustainable. Geothermal water is a highly sought natural resource for electrical power generation and space heating.

Azerbaijan possesses rich geothermal energy and mineral water resources, which can be divided into the following regions [1-7]: Nakhichivan, Greater Caucasus - Pre-Caspian, Lesser Caucasus, Talish mountains, Samur-Devechi piedmont, Absheron peninsula and Kura-Araz depression. More than 50 million m^3 of geothermal energy resources are available in Azerbaijan with maximum temperatures of up to ~140 °C. The geothermal energy and mineral water resources of Azerbaijan can potentially be used for bottled water production, medicinal purposes, for spas and health clinics that utilize the water to treat arthritis, dysfunction of the nervous system and skin diseases.

The geological, geographical and chemical properties of the geothermal resources of Azerbaijan have been extensively studied [1-7]. But, the main thermophysical properties, such as density, viscosity, vapor pressure etc. have only had limited studies. To use the geothermal energy resources of Azerbaijan as an alternative energy source requires the investigation of the thermophysical properties of a wide range of parameters.

The temperature of the geothermal resources of Azerbaijan's part of the Greater Caucasus - Pre-Caspian [(800 to 3385) m] region has approximately 70-100 °C and the estimated discharge is about 4.0 million litres/day. The waters are dominated by sodium-bicarbonate composition. H_2S waters are found on the south and southeast slope of the Greater Caucasus and are confined to sedimentary deposits. Fresh hot calcium-sodium bicarbonate waters were found with temperatures of up to 90 °C. Some geothermal resources have a depth of 1400 m. The waters are imbibed. The main conditions treated are: diseases of the stomach, the liver and biliary ducts, the kidneys and the urethra canal, urology and metabolic disorders. The main chemical components are: Cu, Br, I, F, Mn, Ti, H_2S, Sr etc. [1-3].

The main objective of this paper is to provide accurate experimental density data of the geothermal resources of the second geothermal region of Azerbaijan (Greater Caucasus - Pre-Caspian) at T=(278.15 to 373.15) K and at pressures up to p=40 MPa using a vibrating tube densimeter. For this purpose, the (p,ρ,T) properties of the Palchig-Oba and Mukhtadir geothermal resources of the Khachmaz region have been examined for the first time. Thermodynamic properties of these geothermal resources are not available in the literature and a comparison of them with the literature results was impossible.

The chemical compounds of samples were analysed in the IRIS Intrepid II Optical Emission Spectrometer (U.K.).

The (p,ρ,T) measurements were carried out using a recently developed high pressure–high temperature vibrating tube densimeter DMA HPM (Anton-Paar, Austria) [8-9].

Samples were collected directly from the resources. The Palchig-Oba geothermal resource is at T=352.15 K and Mukhtadir geothermal resource is at T=332.15 K. The geographical coordinates of the resources are:

- Palchig-Oba: 41°32'41" N and 48°43'35" E
- Mukhtadir: 41°66'42" N and 48°78'06" E

The samples were filtered and degassed slowly using the vacuum system. To stop vaporisation of pure water, the vacuum procedure was very slow (the groove of the flask valve, which held the sample, was very slightly opened). We tried to use the samples as close as possible to their original state (T,p), but at the same time to remove all dissolved gases and non-mineral compounds. The amount of dissolved gases or air plays a very negative role in the density measurements, especially at high temperatures.

The chemical compounds analysis of the Palchig-Oba and Mukhtadir geothermal resources were carried-out in the IRIS Intrepid II Optical Emission Spectrometer and the results of analysis are shown in Table 1.

Table1.

Chemical Analysis of the Measured Geothermal Resources

Minerals in the samples in mg/l	Palchig-Oba	Mukhtadir	Minerals in the samples in mg/l	Palchig-Oba	Mukhtadir
Al	<0.01	0.15	Mo	0.02	0.02
As	0.01	0.02	Na	1640	506
B	1.65	1.43	Ni	<0.01	<0.01
Ba	0.54	0.59	P	<0.01	<0.01
Ca	360.0	34.1	Pb	<0.01	<0.01
Cd	<0.01	<0.01	S	41.20	4.74
Co	<0.01	<0.01	Sb	<0.02	<0.02
Cr	<0.01	<0.01	Se	<0.02	<0.02
Cu	<0.01	<0.01	Si	4.79	3.71
Fe	0.01	0.04	Sr	14.40	2.39
Hg	<0.02	<0.02	Ti	<0.01	<0.01
K	22.20	8.04	Tl	<0.05	<0.05
Li	0.33	0.09	V	<0.01	<0.01
Mg	68.60	6.18	Zn	<0.01	<0.01
Mn	0.22	0.08			

The (p,ρ,T) properties of the Palchig-Oba and Mukhtadir geothermal resources of Azerbaijan at T=(278.15 to 373.15) K and at pressures up to p=40 MPa are reported in Table 2.

The measured results were fitted to the equation of state [10] as a function of pressure and temperature

$$p = A(T)\,\rho^{2} + B(T)\,\rho^{8} + C(T)\,\rho^{12}, \qquad (1)$$

where: the coefficients of eqn. (1) A, B and C are functions of temperature.

$$A(T) = \sum_{i=1}^{3} a_i T^{i},\; B(T) = \sum_{i=0}^{2} b_i T^{i},\; C(T) = \sum_{i=0}^{2} c_i T^{i}, \qquad (2)$$

The a_i, b_i and c_i are the coefficients of the polynomials given in Table 3. Eqns. 1-2 describe the experimental results of the investigated Palchig-Oba and Mukhtadir geothermal resources with $\Delta\rho/\rho$= ±0.006 % and $\Delta\rho/\rho$= ±0.005 % average percent deviations, respectively.

Table 2.

Experimental Values of Pressure *p*, Density *ρ*, Temperature *T* of Geothermal Resources of Azerbaijan

p/MPa	ρ/(kg·m^{-3})	T/K	p/MPa	ρ/(kg·m^{-3})	T/K	p/MPa	ρ/(kg·m^{-3})	T/K
				"Palchig-Oba"				
0.786	1007.87	278.21	30.128	1016.85	298.21	15.203	990.72	343.15
5.073	1010.03	278.22	35.104	1018.86	298.20	19.997	992.75	343.15
9.995	1012.29	278.23	40.035	1020.88	298.17	25.004	994.83	343.15
15.101	1014.85	278.22	0.845	999.55	313.15	29.989	996.85	343.16
20.015	1017.13	278.22	5.021	1001.38	313.16	35.207	998.92	343.15
25.229	1019.49	278.22	10.002	1003.52	313.14	39.992	1000.77	343.15
30.097	1021.72	278.21	15.203	1005.72	313.15	1.012	975.14	358.15
34.985	1023.84	278.21	19.996	1007.70	313.15	5.065	977.00	358.16
40.100	1026.15	278.20	25.025	1009.74	313.16	10.025	979.23	358.15
0.958	1006.68	288.24	29.994	1011.72	313.14	15.047	981.47	358.14
5.188	1008.94	288.25	35.024	1013.68	313.15	20.035	983.65	358.15
10.057	1011.10	288.24	39.995	1015.57	313.15	25.621	986.05	358.15
15.089	1013.30	288.23	0.870	993.27	327.11	30.058	987.93	358.16
19.951	1015.39	288.21	5.123	995.18	327.12	35.106	990.03	358.15
24.990	1017.63	288.20	10.042	997.23	327.13	39.985	992.03	358.15
30.037	1019.82	288.18	15.187	999.45	327.14	1.326	965.17	373.12
35.041	1021.84	288.17	19.978	1001.35	327.15	5.108	967.06	373.12
40.010	1023.96	288.15	25.227	1003.53	327.16	10.166	969.29	373.15
1.035	1004.46	298.24	30.096	1005.53	327.16	15.004	971.40	373.18
5.147	1006.43	298.24	35.090	1007.48	327.17	20.071	973.63	373.18
10.054	1008.49	298.23	40.068	1009.26	327.18	25.167	975.87	373.18
14.991	1010.66	298.23	0.924	984.42	343.14	30.106	978.06	373.16
20.021	1012.83	298.22	5.001	986.26	343.15	35.011	980.08	373.17
25.061	1014.86	298.21	10.005	988.47	343.16	40.022	982.21	373.16
				"Mukhtadir"				
0.728	1006.66	278.18	29.997	1014.91	298.18	15.580	989.37	342.49
5.039	1008.67	278.18	35.003	1016.95	298.17	20.090	991.29	342.50
9.963	1010.92	278.18	40.004	1018.95	298.16	25.598	993.55	342.50
15.102	1013.22	278.18	1.594	997.64	313.23	30.083	995.35	342.51
19.985	1015.40	278.18	5.059	999.29	313.19	35.605	997.54	342.51
25.104	1017.66	278.18	10.048	1001.47	313.17	40.124	999.26	342.52
29.968	1019.75	278.18	15.102	1003.59	313.16	0.412	973.51	358.15
35.102	1021.98	278.18	20.083	1005.64	313.16	5.001	975.55	358.14
40.045	1024.10	278.18	25.076	1007.59	313.16	10.026	977.74	358.16
0.731	1005.00	288.11	30.064	1009.51	313.16	15.004	979.88	358.15
5.085	1006.99	288.12	35.102	1011.48	313.16	20.006	982.00	358.17
9.797	1009.08	288.15	40.003	1013.35	313.16	25.014	984.09	358.16
15.100	1011.44	288.15	1.437	990.98	328.12	30.005	986.14	358.15
20.072	1013.59	288.16	5.071	992.56	328.12	35.026	988.16	358.14
25.102	1015.84	288.15	10.004	994.78	328.12	39.998	990.13	358.15
29.980	1017.82	288.17	15.102	996.93	328.12	0.905	963.13	373.75
35.113	1019.99	288.17	20.060	999.00	328.12	4.966	965.15	373.74
40.018	1021.99	288.18	25.133	1000.88	328.13	10.030	967.25	373.76
0.471	1002.27	298.17	30.066	1002.90	328.15	15.600	969.66	373.77
5.077	1004.31	298.18	35.089	1004.79	328.15	19.946	971.74	373.72
10.066	1006.50	298.19	40.008	1006.69	328.16	25.600	974.11	373.73
15.086	1008.66	298.19	0.700	983.08	342.47	29.955	975.91	373.73
20.068	1010.78	298.19	5.098	984.89	342.48	35.604	978.14	373.74
25.086	1012.88	298.18	9.893	987.02	342.48	39.917	980.04	373.70

Figures 1-3 show plots of pressure p of Palchig-Oba geothermal water *vs* density ρ, of density ρ of the "Mukhtadir" geothermal water *vs* temperature T and deviations of experimental density $\rho_{exp.}$ of geothermal resources from the calculated density $\rho_{cal.}$ by eqns. 1-2 *vs* pressure p.

The isothermal compressibility k_T/MPa^{-1} is a measure of the relative volume change of a fluid as a response to a pressure change at constant temperature and has been calculated using the following equations:

$$k_T = (1/\rho)(\partial p/\partial \rho)_T^{-1}, \quad (3)$$

$$k_T = 1/(2A\rho^2 + 8B\rho^8 + 12C\rho^{12}). \quad (4)$$

Table 3.

Values of the coefficients a_i, b_i and c_i in Eqns. 1-2.

a_i	b_i	c_i
Geothermal water "Palchig-Oba"		
a_1= -5.96906137647 a_2= 0.03060188658 a_3= -0.4800227471·10^{-4}	b_0= 7660.5225241 b_1= -49.491673 b_2= 0.0829263	c_0= -5397.473667514 c_1= 35.409651677 c_2= -0.0575229913
Geothermal water "Mukhtadir"		
a_1= -4.7515053754 a_2= 0.016796300766 a_3= -0.180154918·10^{-4}	b_0= 3126.98965826775 b_1= -16.43641168 b_2= 0.024923696862	c_0= -1903.808553421 c_1= 10.726873351 c_2= -0.015075828933

The calculated results shown in Figure 4 *vs* temperature T.

Another thermal property that can be calculated from eqns. 1-2 is the isobaric thermal expansibility α_p/K^{-1}, which is the tendency of matter to change in volume in response to a change in temperature at constant pressure, i.e., the degree of expansion divided by the change in temperature

$$\alpha_p = (1/\rho)(\partial p/\partial T)_\rho (\partial p/\partial \rho)_T^{-1}, \quad (5)$$

$$\alpha_p = [A'(T) + B'(T)\rho^6 + C'(T)\rho^{10}]/[2A(T) + 8B(T)\rho^6 + 12C(T)\rho^{10}], \quad (6)$$

where: $A'(T)$, $B'(T)$, and $C'(T)$ are the derivatives of the $A(T)$, $B(T)$, and $C(T)$ in the following form

$$A'(T) = \sum_{i=1}^{3} i a_i T^{i-1}, B'(T) = \sum_{i=1}^{2} i b_i T^{i-1}, C'(T) = \sum_{i=1}^{2} i c_i T^{i-1} \quad . \quad (7)$$

The next important parameter for the investigation of the thermodynamic properties of geothermal resources is the difference between the specific heat capacities determined at constant pressure and constant volume.

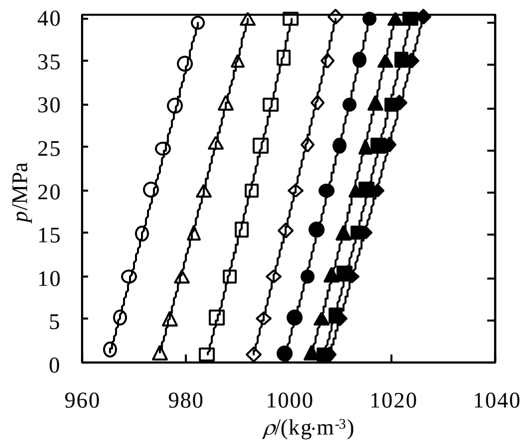

Fig.1.

Plot of pressure p of Palchig-Oba geothermal resources *vs* density ρ: ◆, 278.22K; ■, 288.21K; ▲, 298.22K; ●, 313.15K; ◇, 327.15K; □, 343.15K; Δ, 358.15K; ○, 373.16K; ___ calculated by eqs. 1-2.

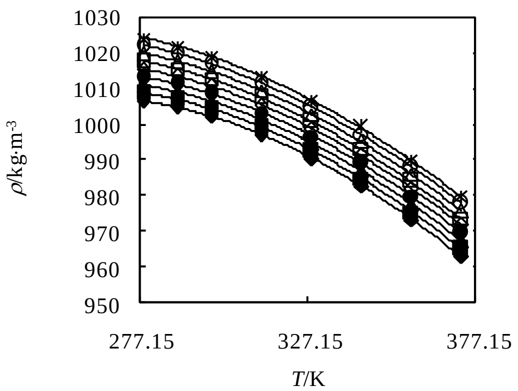

Fig.2.

Plot of density ρ of Mukhtadir geothermal resources *vs* temperature T: ◆, 0.101MPa; ■, 5MPa; ▲, 10MPa; ●, 15MPa; ◇, 2 MPa; □, 25MPa; Δ, 30MPa; ○, 35MPa; *, 40MPa

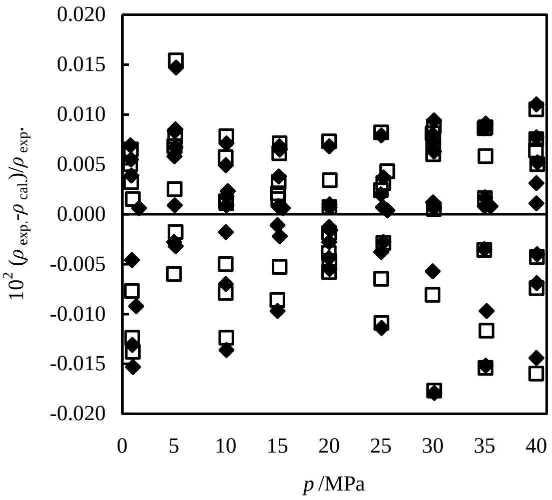

Fig.3.

Plot of deviations of experimental density $\rho_{exp.}$ of the investigated geothermal resources of Azerbaijan from the calculated by eqns. 1-2 density $\rho_{cal.}$ *vs* pressure *p*: ◆, Palchig-Oba and □, Mukhtadir.

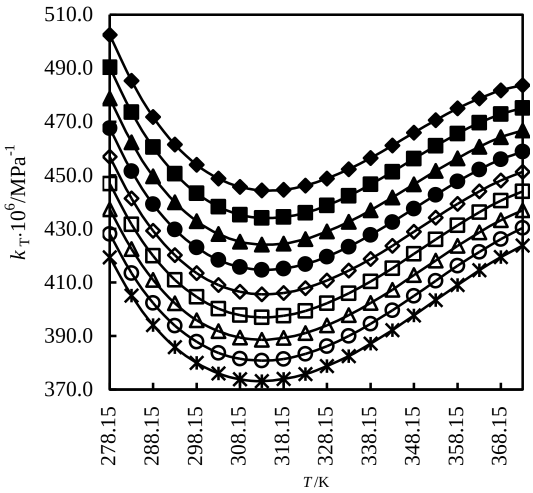

Fig.4.

Plot of isothermal compressibility $k_T \cdot 10^6$/MPa^{-1} of Palchig-Oba geothermal water *vs* temperature *T*: ◆, 0.101MPa; ■, 5MPa; ▲, 10MPa; •, 15MPa; ◇, 20MPa; □, 25MPa; Δ, 30MPa; ○, 35MPa; *, 40MPa.

Measuring the heat capacity at constant volume can be prohibitively difficult for liquids. It is easier to measure the heat capacity at constant pressure and solve for the heat capacity at constant volume using mathematical relationships derived from basic thermodynamic laws

$$c_p = c_v + T\frac{(\partial p/\partial T)_\rho^2}{\rho^2(\partial p/\partial \rho)_T}, \quad (8)$$

where: c_p and c_v are the heat capacities at constant pressure and volume, respectively. From the eqns: (3) and (5)

$$c_p - c_v = \frac{\alpha_p^2 T}{\rho k_T}, \quad (9)$$

From the analysis of the isothermal compressibility values of samples it is apparent that geothermal resources have similar anomalies to those of pure water. This is not very surprising since the majority of resources is pure water. In a typical liquid the compressibility decreases as the structure becomes more compact due to lowered temperature. In water and all aqueous salt solutions in which the concentration of water is very high, the cluster equilibrium shifts towards a more open structure as the temperature is reduced due to preference for a more ordered structure. As the water structure is more open at these lower temperatures, the capacity for it to be compressed increases [11]. The effect is not a simple dependency on density, however, or else the minimum at *T*=319.65 K for isothermal compressibility of pure water. The temperature dependence of isothermal compressibility k_T/MPa^{-1} anomalies presented in Figure 4.

The isobaric thermal expansibility of geothermal resources increases with increased pressure up to about *T*=313.17 K in contrast to most other liquids where thermal expansion decreases with increased pressure. After *T*=313.17 K isobaric thermal expansibility of geothermal resources decreases with increased pressure. This is due to the collapsed structure of water having a greater thermal expansibility than the expanded structure and the increasing pressure shifting the equilibrium towards a more collapsed structure.

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AZƏRBAYCANIN PALÇIQ-OBA VƏ MÜXTƏDİR GEOTERMAL SULARININ TERMODİNAMİK XASSƏLƏRİ

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Təqdim olunan məqalədə Azərbaycanın Xaçmaz rayonunun ərazisində yerləşən Palçıq-Oba və müxtədir geotermal sularının sıxlığının temperatur və təziqdən asılılığı araşdırılmışdır. Təcrübələr T=(278.15-373.15)K temperatur və p=40MPa təziq intervalında aparılmışdır. Alınmış nəticələr əsasında hal tənliyi qurulmuş və tədqiq olunan geotermal suların termiki xassələri hesablanmışdır.

ТЕРМОДИНАМИЧЕСКИЕ СВОЙСТВА ГЕОТЕРМАЛЬНЫХ ВОД ПАЛЧИГ-ОБА И МУХТАДИР АЗЕРБАЙДЖАНА

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Приведены экспериментальные исследования плотности геотермальных вод Палчиг-Оба и Мухтадир Хачмазского района Азербайджана при T=(278.15-373.15)K и давлениях до p=40МПа. Полученные результаты описаны с помощью уравнения состояния и вычислены термические характеристики геотермальных вод.

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