Thermal Diffusivity Prediction From P-Wave Velocity and Porosity Assessment for Sandstone Reservoirs

Abdel Moktader A. El Sayed[1*], Nahla A. El Sayed[2]

[1*] Department of Geophysics, Faculty of Sciences, Ain Shams University, Cairo-Egypt; email: moktader014@gmail.com

[2] Department of Exploration (Core Lab.) Egyptian Petroleum Research Institute-Egypt

http://doi.org/10.29227/IM-2024-01-14

Submission date: *6.2.2023* | Review date: *27.3.2023*

Abstract

Petrophysical heterogeneities of sandstone reservoirs which are generated by rock internal variability resounded to the magnitude of the rock thermal diffusivity. This is expected mostly to variation of rock density, porosity, reservoir temperature and its thermal conductivity. New methodology for calculating thermal diffusivity in a sandstone rock formation is intended and effectively employed some laboratory thermophysical measurements for sandstone reservoirs. The proposed petrophysical model establishes thermal diffusivity if both the effective porosity and acoustic (compressional) wave velocity of the rock are known. Some reliable petrophysical models (El Sayed, 2011 and Ahmed, 2019) concerned to both the Baharyia (Egypt) and Szolnok (Hungary) sandstone formations are used with only some modifications to build an innovative nomography. It permitted precise quantification and determination of the thermal diffusivity for both dry and saturated sandstone samples normalized to reservoir temperature (300K-1060 K). Verification of the proposed model is achieved with applying study cases of laboratory measured thermophysical properties (i.e., porosity, thermal diffusivity/or conductivity and longitudinal wave velocity) for different sandstone types, geological ages and geographic locations. A regression analysis of thermal diffusivity between laboratory measured and predicted data for dry (K-dry) rock samples yield a plausible coefficient of correlations as (R =0.73; 0.86 and 0.98) for three different sandstones obtained from Permo-Carboniferous in Germany (Aretz, 2016) and of dissimilar geologic age in Switzerland (Pimienta, 2018) respectively while, the average standard error equals 0.011. Then again, the laboratory measured and predicted thermal diffusivity (K-sat) of saturated samples display an appropriate coefficient of correlation (R = 0.76) and average standard error (0.0089).

Keywords: thermal diffusivity, p-wave velocity, porosity, sandstone reservoir, egypt

Introduction

Owing to the rise in energy costs and energy need, the energy management and organization must play a significant role in human lives and energy national strategies of most world countries. Heat as a form of energy which could be transferred more quickly in solid medium than in gas and liquid [1] is suitable target for exploration. Consequently, the understanding of the solid materials potential to transfer heat can aid in sustaining energy more efficiently. Thermophysical properties of rocks is an essential parameter in many fields such as constraining the dynamic evolution of planets, exploring the thermal state of basins, and utilizing geothermal resources [2]. It plays a fundamental role in heat transfer in the Earth's interior for determining temperature gradients in the interior of Earth. [3] stated that Information on thermal rock properties is important for many applications ranging from the production of geothermal energy or hydrocarbons (e.g., heavy oils), over subsurface management (e.g., nuclear waste repositories) to civil engineering (e.g., heat transfer or insulation in buildings).Thermal property determination can be classified into two [4] main categories: (1) regression model-based [5-10] and (2) theoretical model-based [11-13]. This is due to the limitations of the existing techniques for in situ rock thermal property measurements in boreholes. Also, the lack of core samples is the main challenge to establish the necessity for techniques of rock thermal property determination based on petrophysical models or even the well-logging data. Thermal recovery is a traditional method for exploiting heavy oil resources. Thermal method of heavy oil recovery persists the most effective method for the development of huge petroleum resources. The most important way to extract heavy oil is to reduce the viscosity of oil and consequently enhance oil mobility utilizing steam injection [14]. Thermal conductivity (λ) and thermal diffusivity (κ) characterize how well a material conducts heat and how fast temperature diffuses in it, respectively. Density (ρ) and specific heat capacity (cp) link these two thermal properties: $\kappa = \lambda/\rho.\ cp$. The heat transfer processes in the hydrocarbon / water reservoir rocks are controlled mainly by the thermal diffusivity. The value of thermal diffusivity of the reservoir media is also changing with temperature which leads to alteration of the heat transfer phenomena in the reservoir. A simple equation describing the relationship between the thermal conductivity (λ) and reservoir temperature (T) was early proposed as:

$$\lambda = 1/A + B \times T \qquad (1)$$

In which (A) and (B), are controlled by the type of lithology, as fitting coefficients. This equation seems to reveal that rocks with a relatively high thermal conductivity exhibit a stronger decrease in (λ) with increasing temperature than those with lower thermal conductivity [2].

[15] developed a model that simulated the heat transfer process in an oil sandstone reservoir where the thermal diffusivity of

the reservoir media is considered as a function of temperature (Ҡ t). The temperature variation at each point of the reservoir is calculated using a heat transfer equation as:

$$(\delta T / \delta t) - \text{Ҡ} (\delta 2T / \delta x2) = 0 \qquad (2)$$

where Ҡ = (λ/ρ. CP) is the thermal diffusivity (mm^2/s), λ is the thermal conductivity (W/m. K), CP is the heat capacity (J/kg· K), and ρ is the density (kg/m^3) of the reservoir rock sample. These parameters are function of temperature, T (x, t). T (x, t) is the reservoir temperature on the distance of x at the given time t, as x is the distance from heat-source, and t is elapsed time.

The use of constant values of the thermophysical parameters (i.e., λ, CP, Ҡ, ρ =constant) instead of their temperature dependencies, λ(T), CP(T), Ҡ(T), in the heat transfer process leads to inaccuracy of the natural reservoir temperature profile, T (x, t) which in turn affecting on the real thermodynamic conditions in the reservoir and the process of oil or geothermal energy recovery. The pressure dependence of the thermal diffusivity, heat capacity and thermal conductivity are negligibly small and can be ignored (Abdulagatov, et al.,2021). The experimental thermal conductivity data can be correctly described high temperature behaviour is introduced by [15] as:

$$\lambda(t) = A + B/Tm \qquad (3)$$

where optimal values of fitting parameters are m=1.5, A=1.705757 $W \cdot m^{-1} \cdot K^{-1}$, and B=26,451.585231 $W \cdot m^{-1} \cdot K^{-2.5}$.

The main goal of the present work is to provide a new model to predict the thermal diffusivity (Ҡ t) from porosity and P-wave velocity. Thermal diffusivity, (Ҡ(t) = λ(t)/ ρ. CP(t) were calculated in the present work as a function of temperature ranged from 300K up to 1060K.

Methodology

The petrophysical parameters as porosity and P-wave velocity were measured [16] at the Petrophysical Lab. of Ain Shams University (Egypt). The plug samples were drilled in the pay zone of the studied formations from the obtained full diameter cores using diamond drill bit and simulated drilling fluids as a bit coolant. The simulated drilling fluid has the same salinity as the formation water. The drilled plug samples were trimmed to form right cylinders. Both sample dimensions are measured within 0.01 mm. The two end surfaces of each sample are ground parallel to within 0.01 mm and numbered using Indian ink. The studied samples were drilled as 2.5 cm diameter, while some samples were drilled later from the original samples for heat capacity measurements to adjust the holder [17] of the used apparatus (LIAG-Institute, Hanover, and Federal Institute of Geosciences and Natural resources (BGR), Hanover). Prior to laboratory measurements the original liquids had been removed from the core samples by washing using Soxhlet extraction technique utilizing suitable organic solvents. While the residual salts were removed using Methyl alcohol [18-20]. The thermophysical parameters of the sandstone samples obtained from both the Szolnok and the Baharyia formations, encountered at depths from (1700 to 3550 m) respectively, have been measured with laboratory devices operated by LIAG-Institute, Department of Geothermal Energy, Hanover, and Federal Institute of Geosciences and Natural resources (BGR), Hanover.

In the present work the sandstone thermal conductivity was measured using the optical scanning method (TCS). A special device is produced by Lippmann and Rauen and based on the contactless optical scanning of the plane of a sample with a focused, mobile heat source in combination with infrared temperature sensors. The principle was developed by [21]. The determination of the thermal conductivity is based on the comparison of temperatures of the standard with unknown samples. The sample is prepared as cylinder and dried in an electric oven for approximately 10 h at 110 °C. The plane area which will be exposed to the thermal beam should be painted black to insure a uniform heat reflection [17]. The thermal conductivity of rocks in general decreases with temperature, in contrast to some amorphous or fused materials such as obsidian. Thermal conductivity was determined of all sandstone rock samples at ambient temperature of 25 °C with optical scanning technique. Thermal conductivity depends largely on mineral content [22], porosity [23], and saturating fluid [24]. The geometric mean model based on mixing laws is considered, as follows:

$$\lambda s = \lambda f \text{Ø} x \lambda m (1 - \text{Ø}) \qquad (4)$$

Where: (λ_f) is the thermal conductivity of the fluid (air or water) present in the porosity (Ø), and λ_m (W/m K) is the thermal conductivity of the solid matrix. The thermal conductivity of water (0.6 $W m^{-1} K^{-1}$) and the thermal conductivity of air (0.02 $W m^{-1} K^{-1}$). Thermal diffusivity (Ҡ t) of some sandstone samples is calculated according to the laboratory measurements using LFA technique and introduced by [15, Table-1]. By using these data [15], the regression line equation is obtained as:

$$\text{Ҡ}(t) = 7.2133e - 0.003K \quad , \quad R^2 = 0.9287 \qquad (5)$$

Where Ҡ(t) = thermal diffusivity, mm^2/s, K=Kalvin. The normalized Ҡ(t) in the present work and CP(t), are calculated using the empirical equation introduced by [17] for sandstone samples of the Baharyia and Szolnok formations:

$$CP(t) = 0{:}0008Tp + 0.7484 \quad , \quad R^2 = 0.9682 \qquad (6)$$

The thermal conductivity (λ t) is assessed using the above listed equation (3) approved by [15]. Subsequently, the relationship between λ t and Ҡ t, is made to calculate the regression line relation controlling them (Fig. 1) as:

$$\text{Ҡ} t = 2.8541 \lambda t - 2.7176 \qquad R^2 = 0.959 \qquad (7)$$

[17, 25-28]) show that porosity is the main controlling factor for permeability, thermal conductivity, and acoustic wave velocity. In the present work, we borrowed the petrophysical model approved by [27] connected to both Baharyia and Szolnok formations and represented by (equation -8) of [27] as:

$$Log\ Ø\ =\ -\log \lambda d - 0.22 \log V\,p - 0.197 \qquad ,R^2\ =\ 0.92 \qquad (8)$$

We solve eq. (8) with eq. (9) by substituting the value of (λ d by λ t at ambient temperature of 25 °C) as:

$$\lambda\, d\ =\ (\text{Ꝁ}\, t\ + 2.7176)/2.8541 \qquad (9)$$

subsequently, the eq. (8) become as:

$$Log\ \text{Ꝁ}\, t\ =\ -\log Ø - 0.22 \log V\,p\ -\ 0.261613 \qquad (10)$$

Furthermore (Ꝁ t) is calculated from porosity and P-wave velocity using Eq. (10). The existing nomography is accomplished between laboratory measured porosity (Ø) and calculated Ꝁ t (eq.-10) at different longitudinal wave velocity (V p) for all studied samples from both Baharyia (Upper Cretaceous, Egypt) and Szolnok (Miocene – Pliocene, Hungary) formations.

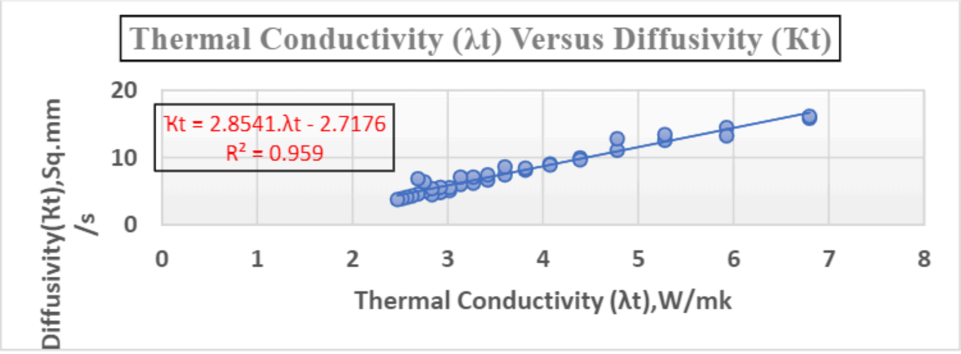

Fig. 1. (λ t) Versus (Ꝁ t) for Bah. And Szolnok formations

Results and discussions

The nomography (Fig. 2) is designed by applying Eq. (10) representing measured and empirical results of the studied sandstone samples belonging to both Baharyia and Szolnok formations of different geological ages, geologic provinces, and geographic location but they are similar in lithology and environment of deposition (both is of deltaic- submarine fan deposits). In this diagram, we have three reservoir parameters (Ø f, Ꝁ d- t and V p) and if you have two values out of the three parameters then you can detect the third. Therefore, we can predict Ꝁ t- d from fractional porosity at certain V p value.

Model Verification

To verify the present model, we used published laboratory measured data for sandstone as a widespread reservoir sample collected among different areas either in Germany, Switzerland, or France ([3], Table-2). In addition, the laboratory measured data of outcrop sandstone samples of Permo-carboniferous geothermal sandstone reservoir formations (Northern Upper Rhine Graben, Germany, ([29], Table-3) are used. Authors studied the impact of mineral content, depositional environment, and diagenesis on sandstone petrophysical properties and thermal diffusivity.

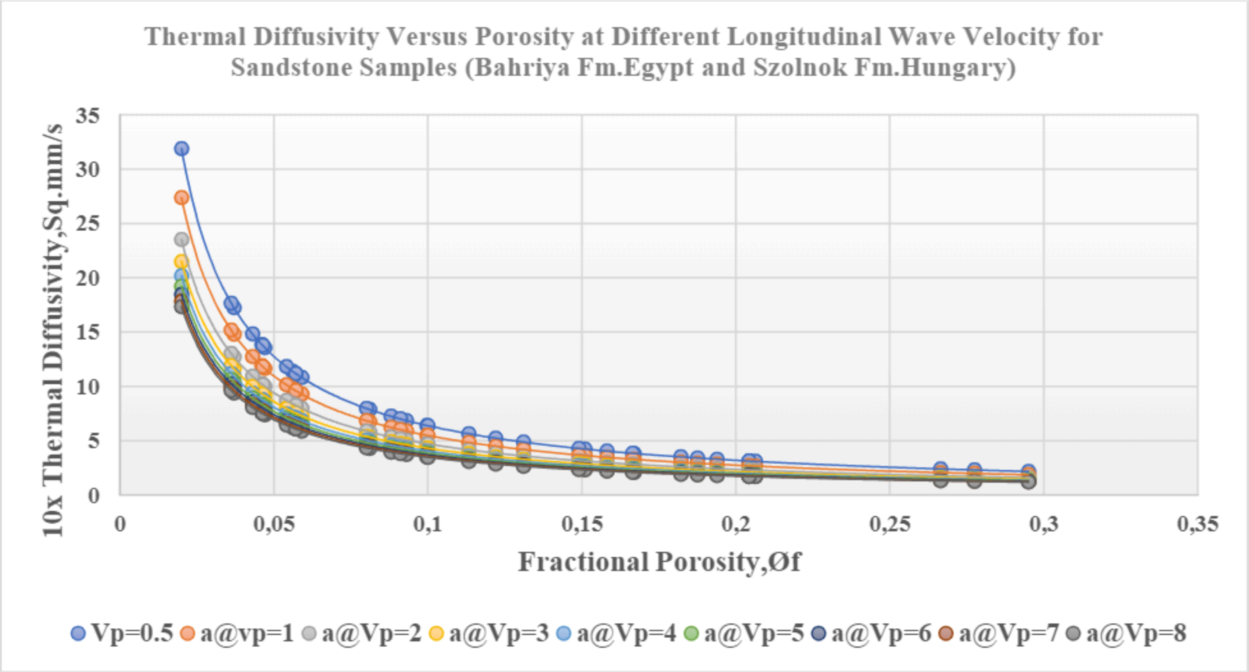

Fig. 2. New Nomography for Predicting Thermal Diffusivity from Porosity and Seismic Velocity

Relationships Between Measured and Calculated Diffusivity

4.a- For dry sandstones:

The relationship between laboratory measured thermal diffusivity and its calculated values using equation (10) for the dry sandstone samples displays three positive polynomial trends (Fig. 3). They are controlling with coefficients of correlation (R =0.73; 0.86 and 0.98) for the three different sandstones ed from dissimilar geologic age in Switzerland [3] and of the Permo-Carboniferous age in Germany [29] respectively.

The equations estimated for these relations are:

For the subsurface sandstone samples of [29].

$$\text{Ƙ}\,dp = -0.5634\,(\text{Ƙ}d)^{2} + 3.4412\text{Ƙ}d - 2.8592 \qquad ,R = 0.98 \qquad (11)$$

For the exposed sandstone samples of [29].

$$\text{Ƙ}\,dp = -0.7035\,(\text{Ƙ}d)^{2} - 2.1\text{¯}32\text{Ƙ}d + 2.2333 \qquad ,R = 0.86 \qquad (12)$$

And for the subsurface sandstone samples of [3].

$$\text{Ƙ}\,dp = -0.8104\,(\text{Ƙ}d)^{2} - 1.9786\text{Ƙ}d + 1.6327 \qquad ,R = 0.73 \qquad (13)$$

Among these calculated equations the Eq. (11) is the most significant and more reliable to predict Thermal diffusivity for dry sandstones due to its higher coefficient of correlation (R= 0.98).

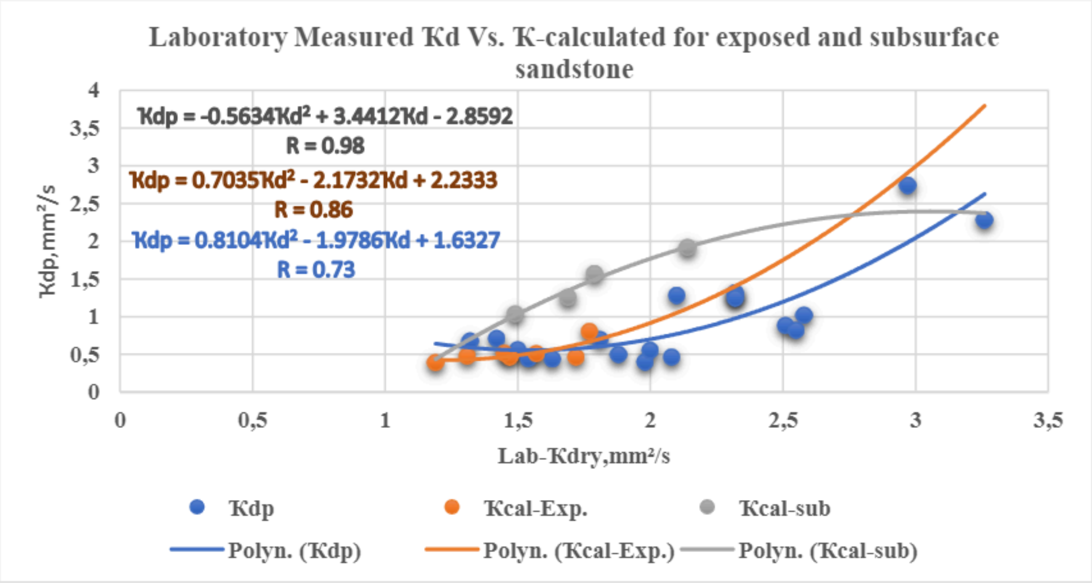

Fig. 3. Laboratory Measured Ƙ d Versus Ƙ-Calculated for sandstone.

4.b- Standard Error of the Ƙ- d:

The thermal diffusivity (Ƙ d) standard error for the dry sandstone samples is calculated. Thereinafter Ƙ d- standard Error frequency histogram is made (Fig. 4). It displays unimodal positive skewed distribution as most of the studied samples (15) have a standard error of 0.006982 while, only one sample has the value of 0. 01658.The cumulative frequency curve indicates that 99% of the studied samples have a very small value (std. err. = 0.0021). The standard error graphical mean (50%) equals to 0.00698. This allows to calculate diffusivity of dry sandstones samples using the present nomography with appropriate precision.

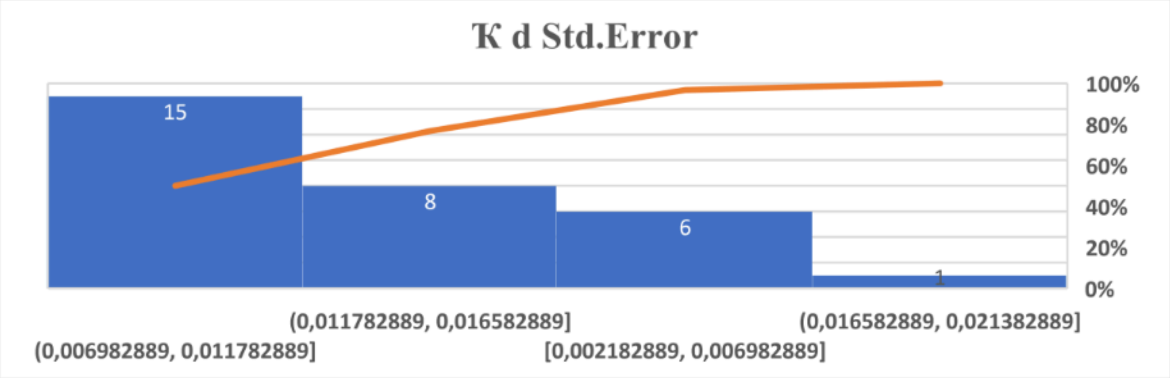

Fig. 4. Frequency Polygon of Ƙ d Standard Error.

4.c- For Saturated Sandstones:

Thermal diffusivity of saturated samples is laboratory measured by [3]. They are used side by side with their predicted values and plotted as (Figure5). The relationship (Fig. 5) shows polynomial trend controlling by the following equation.

$$Ƙsat\ p = 0.9573\,(Ƙsat)^2 - 3.8821Ƙsat + 4.3277 \quad ,R = 0.76 \qquad (14)$$

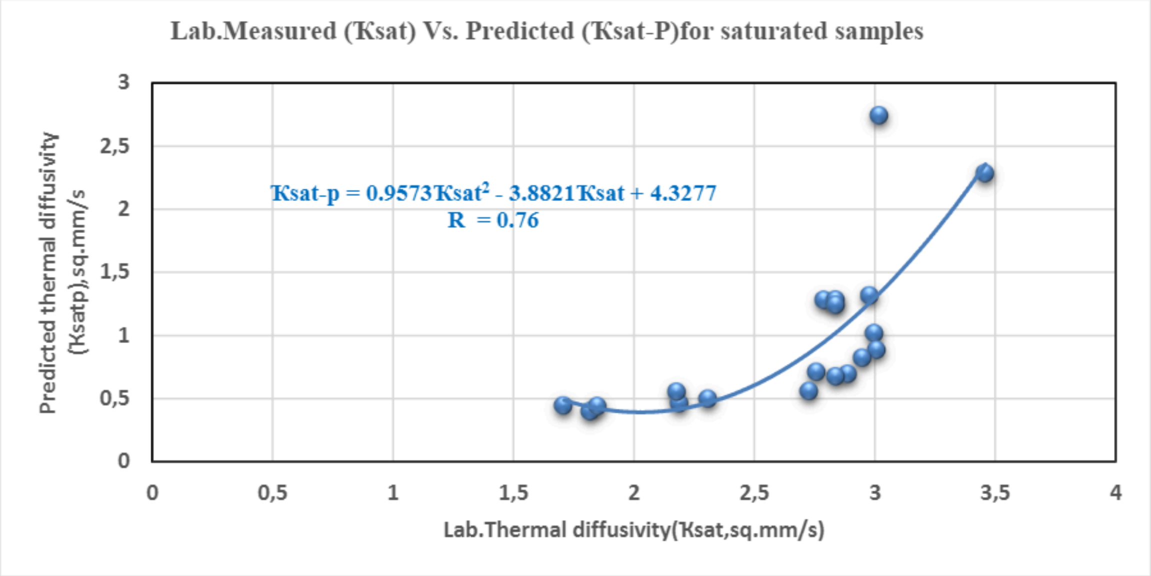

Fig. 5. Lab. Measured (Ƙsat) Vs. Predicted (Ƙsat-P) for saturated samples.

The calculated Eq. (14) could be applied to estimate thermal diffusivity of water saturated sandstone reservoirs.

2.d- Standard Error of the Ƙ- sat:

The standard error frequency polygon (Fig. 6) of the Ƙ- sat displays unimodal positive skewed distribution, as 98% of studied samples have standard error < or = 0.021. The standard error graphical mean (50%) equals to 0.015. This makes available to calculate the thermal diffusivity of water saturated sandstone samples using the Eq. (14) with suitable accuracy.

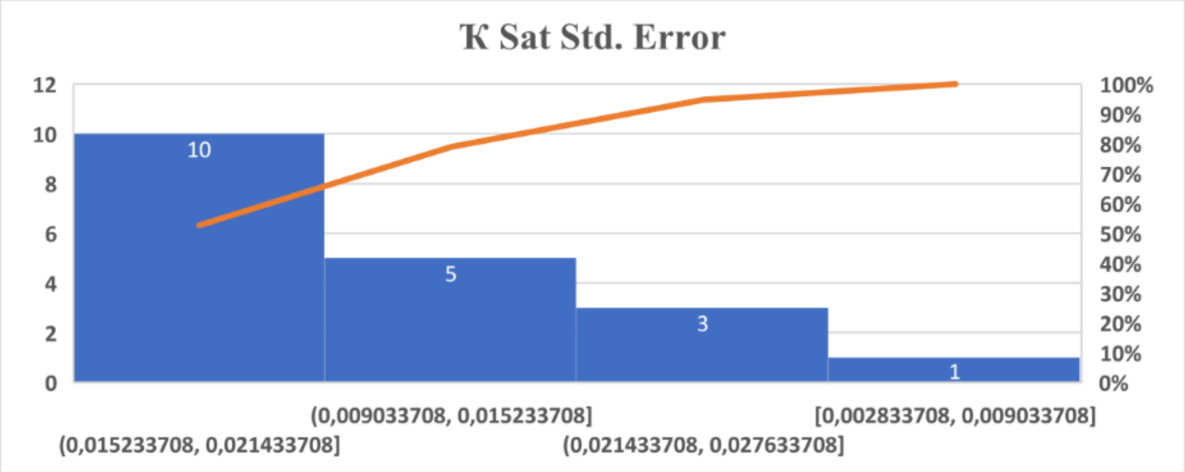

Fig. 6. Frequency Polygon of Ƙ sat- Standard Error.

For Thermal Diffusivity Ƙ(T)

The thermal diffusivity Ƙ(T) is calculated as a function of reservoir temperature (300-1060 K) using equation (5). It is plotted against the thermal diffusivity of sandstone samples studied by [3, 29]. Fig. 7 exhibits a plausible coefficient of correlation (R=0.7904). The relation shows a polynomial trend controlling by the equation:

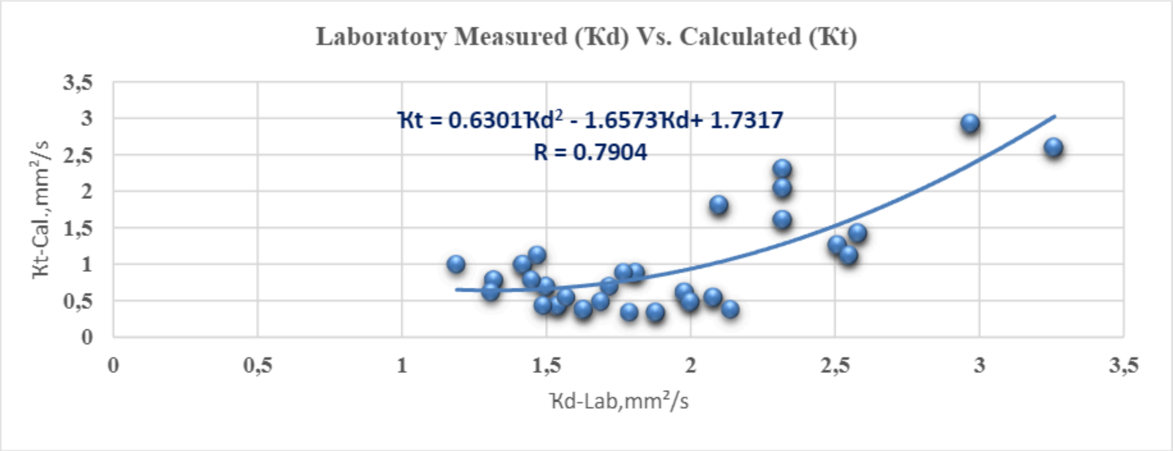

Fig. 7. Laboratory Measured Diffusivity (Ꝁ d) Vs. Cal. Ꝁ(T)

$$Ꝁt = 0.6301\,(Ꝁd)^2 - 1.6573Ꝁd + 1.7317 \qquad ,R = 0.79 \qquad (15)$$

Normalized thermal diffusivity (Ꝁ t) standard error is presented in Fig. 8). It shows skewed distribution with blocks range in relative frequencies from 20.41% up to 28.57%. It displays that 90% of studied samples have standard error of < or = 0. 0095.The standard error of 80% of samples is of 0.00013.

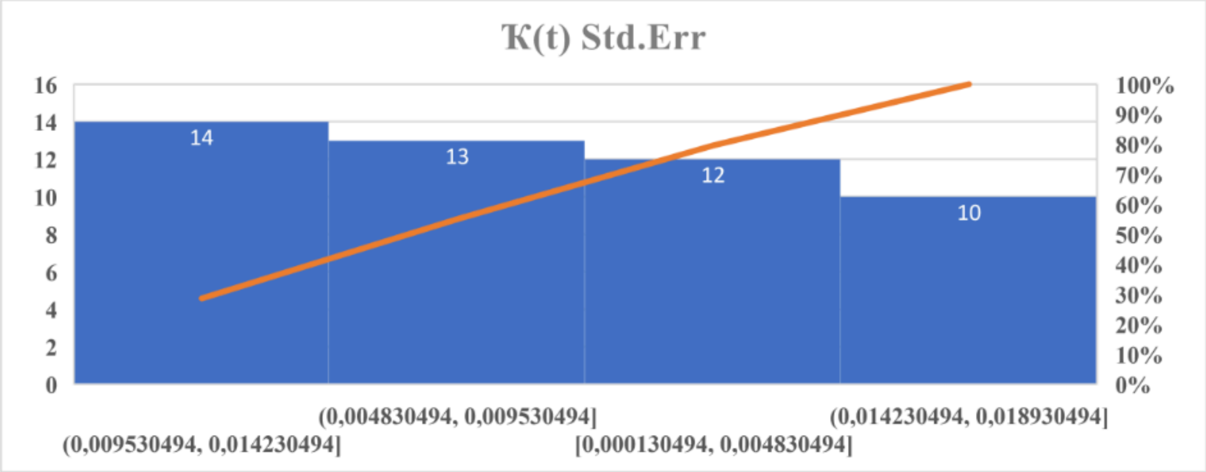

Fig. 8. Frequency Polygon of Ꝁ (t) Standard Error.

This indicates that the calculated Eq. (15) utilizes to estimate normalized sandstone diffusivity (Ꝁ t) as function of reservoir temperature.

Conclusion

1. New methodology for calculating thermal diffusivity in a sandstone rock formation is intended and effectively employed some laboratory thermophysical measurements for sandstone reservoirs.
2. Some reliable petrophysical models [17, 27] concerned to both the Baharyia (Egypt) and Szolnok (Hungary) sandstone formations are used with only some modifications to build an innovative nomography.
3. Verification of the proposed model is achieved with applying study cases of laboratory measured thermophysical properties (i.e., porosity, thermal diffusivity/or conductivity and longitudinal wave velocity) for different sandstone types, geological ages and geographic locations.
4. A regression analysis of thermal diffusivity between laboratory measured and predicted data for dry (Ꝁ-dry) rock samples yield a plausible coefficient of correlations as (R =0.73; 0.86 and 0.98) for three different sandstones obtained from Permo-Carboniferous in Germany (Aretz et al.,2016) and of dissimilar geologic age in Switzerland (Pimienta et al.,2018) respectively.

The regression line equations (Eq.11 up to Eq.15) are calculated for dry sample's diffusivity, saturated and at reservoir temperature Ꝁ(T) prediction respectively.

References

1. Samaei, M., Massalow, T., Abdolhosseinzadeh, A., Yagiz, S., Muayad, M., Sabri, S.,2022. Application of Soft Computing Techniques for Predicting Thermal Conductivity of Rocks. MDPI,Basel,Switzerland.Appl.Sci.2022,12,9187.https://doi.org/10.3390/app12189187
2. Chi Chen, Chuanqing Zhu, Baoshou Zhang, Boning Tang, Kunyu Li, Wenzheng Li, and Xiaodong Fu.,2021. Effect of Temperature on the Thermal Conductivity of Rocks and Its Implication for In Situ Correction. Hindawi Geofluids Volume 2021, Article ID 6630236, 12 pages https://doi.org/10.1155/2021/6630236
3. Pimienta, L. Klitzsch, N., Clauser, C.,2018. Comparison of thermal and elastic properties of sandstones: Experiments and theoretical insights. Geothermics76 (2018) 60-73, https://doi.org/10.1016/j.geothermics.2018.06.005
4. Shakirov, A., Chekhonin E., Popov, Yu. Popov, E., Spasennykh, M., Zagranovskaya, D., Serkin, D.,2021. Rock thermal properties from well-logging data accounting for thermal anisotropy.Geothermics92(2021) 102059. https://doi.org/10.1016/j.geothermics.2021.102059
5. Goss, R., Combs, J., Timur, A., 1975. Prediction of thermal conductivity in rocks from other physical parameters and from standard geophysical well logs. In: SPWLA 16th Annual Logging Symposium. SPWLA-1975-MM, p. 21.
6. Vacquier, V., Mathieu, Y., Legendre, E., Blondin, E., 1988. Experiment on estimating thermal conductivity of sedimentary rocks from oil well logging. Int. J. Rock Mech. Min. Sci. (1997) 26 (2), 63–63.
7. Blackwell, D., Steele, J., 1989. Thermal Conductivity of Sedimentary Rocks: Measurement and Significance. Springer. https://doi.org/10.1007/978-1-4612-
8. Leu, W., Rybach, L., Scharli, U., Megel, T., Keller, B., 1999. New thermal property data base of the Swiss Molasse Basin sediments: integrating wireline logs, cores and cuttings. Proc. Eur. Geothermal Conf. Baset 2, 213–219.
9. Fuchs, S., Balling, N., Forster, ¨ A., 2015. Calculation of thermal conductivity, thermal diffusivity and specific heat capacity of sedimentary rocks using petrophysical well logs. Geophysics. J. Int. 203 (3), 1977–2000. https://doi.org/10.1093/gji/ggv403
10. Zimmerman, R.W., 1989. Thermal conductivity of fluid-saturated rocks. J. Petrol. Sci. Eng. 3 (3), 219–227
11. Beardsmore, G., Cull, J., 2001. Crustal Heat Flow: A Guide to Measurement and Modelling. Cambridge University Press, p. 324. https://doi.org/10.1017/ CBO9780511606021.
12. Hartmann, A., Rath, V., Clauser, C., 2005. Thermal conductivity from core and well log data. J. Rock. Mech. Min. Sciences 42 (7), 1042–1055.
13. Clauser, C., 2020. Thermal storage and transport properties of rocks, II: thermal conductivity and diffusivity. In: Gupta, H.K. (Ed.), Encyclopedia of Solid Earth Geophysics. Springer International Publishing, Cham, pp. 1–20. https://doi.org/ 10.1007/978-3-030-10475-7_67-1.
14. Ali, S.F.,2003. Heavy oil—ever more mobile J. Pet. Sci. Eng. 37, 5 (2003).
15. Abdulagatov, I. Abdulagatov, Z., Grigor'ev, B., Kallaev, S., Omarov, Z., Bakmaev, A., Ramazanova, A., Rabadanov, K., 2021. Thermal Diffusivity, Heat Capacity, and Thermal Conductivity of Oil Reservoir Rock at High Temperatures. International Journal of Thermo-physics (2021) 42:135. https://doi.org/10.1007/s10765-021-02878-x
16. El Sayed, A.M.A., et al., 2019. IOP Conf. Ser.: Earth Environ. Sci. 221, 012046.
17. El Sayed, A.M.A., 2011. Thermophysical study of sandstone reservoir rocks. J. Pet. Sci. Eng. 76, 138–147.
18. Keelan, D.K., 1972. Core Analysis Techniques and Applications. SPE-4160. Nov. pp. 72.
19. El Sayed, A.M.A.,1976. Petrophysical studies on core samples from Um El Yusr oil field, Eastern Desert, Egypt. M.Sc. Thesis, Ain Shams University, Cairo, P.1-137.
20. API, 1998. Recommended Practices for Core Analysis, Recommended Practice 40, 2nd ed. API Publishing Services, Washington.
21. Clauser, C., Griess Haber, E., Neugebauer, H.J., 2002. Decoupled thermal and mantle helium anomalies: implication for the transport regime in continental regime rift zones. J. Geophysics. Res. 107, 2269. https://doi.org/10.1029/2001JB000675.

22. Fuchs, S., Förster, A., 2010. Rock thermal conductivity of Mesozoic geothermal aquifers in the Northeast German Basin. Chimei der Erde 70 (Suppl. 3), 13–22.
23. Tong, F., Jing, L., Zimmerman, R.W., 2010. A fully coupled thermo-hydro-mechanical model for simulating multiphase flow, deformation and heat transfer in buffer material and rock masses. Int. J. Rock Mech. Min
24. Jorand, R., Fehr, A., Koch, A., Clauser, C., 2011. Study of the variation of thermal conductivity with water saturation using nuclear magnetic resonance. J. geophysics. Res.: Solid Earth 116, B8.
25. Mielke, P., Weinert, S., Bignall, G., Sass, I., 2016. Thermo-physical rock properties of greywacke basement rock and intrusive lavas from the Taupo Volcanic Zone, New Zealand. J. Volcano. Geotherm. Res. 324, 179–189.
26. Mielke, P., Bär, K., Sass, I., 2017. Determining the relationship of thermal conductivity and compressional wave velocity of common rock types as a basis for reservoir characterization. J. Appl. geophysics. 140, 135–144.
27. El Sayed, A. M. A., El Sayed, N.A.,2019. Thermal conductivity calculation from P-wave velocity and porosity assessment for sandstone reservoir rocks. Geothermics. 82 (2019) 91-96. https://doi.org/10.1016/j.geothermics.2019.06.001.
28. Ahmed, Z., Yves, G., Marc, D., Kamel, B., 2019. A Preliminary study of relationships between thermal conductivity and petrophysical parameters in Hamra Quartzites reservoir, Hassi Messaoud field (Algeria). J. Afr. Earth Sci. 151, 461–471. https://doi. org/10.1016/j.jafrearsci.2019.01.005.
29. Aretz A., Bär K., Götz A., Sass, I., 2016. Outcrop analogue study of Permo-Carboniferous geothermal sandstone reservoir formations (northern Upper Rhine Graben, Germany): impact of mineral content, depositional environment and diagenesis on petrophysical properties. Int J Earth Sci (Geol Rundsch) (2016) 105:1431–1452 DOI 10.1007/s00531-015-1263-2.