

September 2021 Vol.64 No.9: 1947–1952 https://doi.org/10.1007/s11431-021-1884-1

Leakage detection of oil tank using terahertz spectroscopy

QIN FanKai^{1,2}, CHEN SiTong^{1,2}, CHEN Ru^{1,2}, ZHAN HongLei^{1,2,3}, MIAO XinYang^{1,2,3}, XIANG WenFeng^{2,3} & ZHAO Kun^{1,3,4*}

¹ College of New Energy and Materials, China University of Petroleum, Beijing 102249, China;

² Beijing Key Laboratory of Optical Detection Technology for Oil and Gas, China University of Petroleum, Beijing 102249, China; ³ Key Laboratory of Oil and Gas Terahertz Spectroscopy and Photoelectric Detection, Petroleum and Chemical Industry Federation,

China University of Petroleum, Beijing 102249, China;

⁴ Detection and Beijing Key Laboratory of Failure, Corrosion, and Protection of Oil/Gas Facilities, China University of Petroleum, Beijing 102249, China

Received March 11, 2021; accepted June 24, 2021; published online August 10, 2021

The necessity for safety in oil-gas storage and transportation has led to increasing technical requirements for on-line monitoring of damaged pores and oil leakage from tanks. In this study, the severity of damage of the oil tank at the micron level was detected by terahertz time-domain spectroscopy (THz-TDS), which is of great significance for the early detection and prevention of oil leakage. The THz amplitude (E_p) was related to the severity of damaged according to the THz-TDS measurement of oil tanks with various degrees of damage, including intact, partially damaged, completely damaged, and seriously damaged points. Absorption and scattering effects co-occurred when the THz wave penetrated the tanks, with the collective tendencies being used to expressly monitor oil leakage from tanks. When the oil tank was damaged to form micron-level pores and the crude oil had not overflowed, the pore size was close to THz wavelength and the Mie scattering effect was obvious. After further destruction of the pores, the crude oil gradually spilled over and the scattering effect was gradually transformed from Mie scattering to Rayleigh scattering. In addition, the polar molecules in crude oil have strong resonance under the irradiation of THz wave, and the THz wave has strong attenuation. Eventually, surface tension of the oil flattens the surface of the tank, the scattering effect is gradually suppressed and replaced by the absorption effect. Absorption and scattering caused by THz waves passing through tanks coexist and have competing relationships. The change rule of $E_{\rm P}$ can successfully prove the phenomenon and can be considered as an important alternative for application to predict the degree of tank damage. Therefore, in this study, the detection of pores as small as micrometers on the oil tank was expected to greatly prevent oil leakage accidents and improve the safety of oil and gas storage and transportation.

absorption, scattering, terahertz spectroscopy, oil tank, leakage

Citation: Qin F K, Chen S T, Chen R, et al. Leakage detection of oil tank using terahertz spectroscopy. Sci China Tech Sci, 2021, 64: 1947–1952, https://doi. org/10.1007/s11431-021-1884-1

1 Introduction

Because oil tanks are essential for oil-gas storage and transportation, safety assessment was a significant subject in this field. As the continuous oil corrosion and the sediment erosion, the damaged pores on the tank gradually expand, which may cause oil leakage accidents if the damaged pores were not detected early. The minimum pore diameter is usually in hundreds of micrometers or several millimeters when crude oil leaks from oil tanks, but the current commonly used technology is usually limited to detecting millimeter-scale pores. In order to achieve the purpose of early detection and prevention of oil leakage, this study focus on the detection of micron-scale damages. The detection of

^{*}Corresponding author (email: zhk@cup.edu.cn)

[©] Science China Press and Springer-Verlag GmbH Germany, part of Springer Nature 2021

micron-scale pores on oil tanks is significant to reduce economic losses and avoid environmental pollution [1-4].

It was challenging to accurately measure severity of oil tank damage because of many factors, including human error, oil temperature, and equipment resolution [5-7]. A variety of measurement methods have been put forward to diagnose the severity of damage. As the most widespread and fundamental measurement method, manual measurement of the liquid level's height in the oil tank was an essential part of the safety assessment. Although this method operated efficiently, it was substantially affected by human error and oil temperature. It was challenging to find the micron-sized pores that were damaged on the tank. Tracer detection was another standard technology to diagnose the severity of damage of the oil tank. Tracer detection involves injecting the tracer into the bottom of the oil tank and detecting the tracer outside the oil tank. The advantages of this technology included high resolution (micron-scale) and low cost, but it may damage the oil tank and pollute oil during the operation [8–10].

In the last decade, acoustic emission testing (AET) has been applied throughout the petrochemical industry [11,12]. Transient elastic waves were generated in the process of material deformation. AET was used to detect, record, and analyze the transient elastic waves and deduce the AE source (oil tank) characteristics. The main advantages of AET include high resolution, real-time monitoring, and non-destructive testing. However, it was affected by the environment such as electromagnetic interference, noise of the fluid in the oil tank, rainfall, and wildlife or birds perching on the tanks [13–15].

A non-destructive testing technology with a high signal-tonoise ratio and high sensitivity was required to detect the severity of damage to oil tanks. As an optical technology, THz-TDS had strong applicability in the oil field because of its non-contact testing and intense interaction with organic matter and water [16-18]. In general, a photon is readily absorbed when it has a similar energy level to the vibration and rotation modes of the molecule. The vibration, rotation, and transition frequencies of most organic compounds in oil overlapped with the THz band [19]. When the THz wave propagates in pores on oil-bearing rocks, the attenuation of THz signal was primarily contributed by the absorption and the scattering effect, which scattering is the major factor [20]. According to the study of THz wave scattering by mineral particles, the smaller particles (tens of micron) behave as Rayleigh particles in the THz band, while larger particles (hundreds of micron) behave as Mie particles. The attenuation of THz signal increases with increasing the size of the particles [21]. THz-TDS technology has been applied to detect the disaggregation of crude oil in a magnetic field, evaluate the oil-water two-phase flow, and probe the pattern transitions of the oil-water two-phase flow [22–24].

THz-TDS technology has numerous practical applications in the field of oil-gas storage and transportation, but it has not been applied to directly detect the leakage of crude oil to make more contributions to the safety of this field. In this study, the severity of damage and oil leakage of simulated oil tanks are detected by THz-TDS. The results suggest that THz-TDS was a practical and sensitive technology for the safety detecting of oil tank. It is meaningful for the safety in oil-gas storage and transportation.

2 Experimental

The experimental equipment consisted of a transmissiontype THz-TDS system and a mode-locked femtosecond (fs) Ti-sapphire laser (MaiTai) at repetition rates of 80 MHz, as shown in Figure 1(a). The fs laser beam with a center wavelength of 800 nm is split into a pump beam and a probe beam by a polarization beam splitter (PBS). The THz wave is generated with a GaAs photo-conductive antenna activated by the pump beam. The probe beam detects an electro-optic



Figure 1 (Color online) (a) Experimental setup of THz-TDS measurement; (b) four types of pores.

effect through a detector made up of a ZnTe crystal. In addition, the delay unit can change time delay between THz pulse and probe laser so that TDS, THz electric field as a function of time, can be detected. The spot of the equipment used in this experiment is 1 mm. Since water molecules can absorb THz waves, THz-TDS technology is affected by air humidity. Therefore, the air environment is first tested as a reference signal before each detection. The THz-TDS was obtained in a atmospheric environment with a humidity of 20% at 25°C.

Before using the THz-TDS technology to study the severity of damaged pores and oil leakage, it is necessary to reduce the influence of the oil tank material on the THz wave. Therefore, in this paper, the polyethylene (PE) material which is almost transparent in THz band was selected to simulate the oil tank. The oil tank is a cuboid with a size of 100 mm×20 mm×10 mm, and the thickness is 3 mm. The crude oil sample used in this experiment was obtained from Venezuela with a viscosity of 540.89 mPa S and a wax content of 0.01%. The diameter of the damaged pores on the oil tank studied in this experiment is about 100 microns. The pores on the oil tank are round, and as the severity of damage increases, the pores gradually deepen, and the crude oil leaks more. According to the depth of damage, oil tanks were classified into four types: intact, partially damaged, completely damaged, and seriously damaged, as shown in Figure 1(b). For partially damaged pore, the oil tank had been not penetrated and the depth of the pore was less than 3 mm, thus there was no oil overflow. As the depth of the pore reached 3 mm, oil spilled out of the tank and filled the pore, but there was no major leak, which was regarded as a completely ruined pore. When the oil tank was penetrated and a large amount of oil had overflowed, the severity of destroying was defined as the seriously damaged. When THz wave irradiates the damaged pore on oil tank, the scattering effect occurs. If the pore is filled with oil, the oil will absorb THz wave and suppress the scattering effect.

3 Results and discussion

Initially, a fundamental characterization of the THz dielectric effects of 14 oil tanks was conducted, representing four types of damage. The inset at the top of Figure 2 demonstrated a function of time and THz signal E_P . It was apparent that the THz signal changed with the severity of damage of the oil tank from two aspects, E_P and time delay (τ). The E_P for 14 oil tanks was extracted from the measured THz waveforms to build a relationship between the transmitted signal and the damaged severity of oil tanks.

The symbol-line graph in Figure 2 showed the E_{PS} of 14 oil tanks. The E_{PS} were divided into four types that matched of the severity of damage. An increase in severity of damage



Figure 2 (Color online) THz-TDS and E_p for four types of damaged severity.

was related to a downward trend in the $E_{\rm P}$ and was divided into three stages.

The $E_{\rm P}$ decreased from 0.0074 to 0.0053 V during the first stage when the oil tank changed from intact to partially damaged. This may be owning to the scattering occurred while the surface of the oil tank became rougher with an increase of severity of damage [25-29]. For the second stage, the oil gradually overflowed because of the oil tank's change from partial damage to complete damage. As the oil leakage increased, the intensity of absorption effects increased; meanwhile, the oil tank's surface gradually flattened, and the intensity of scattering effects decreased. Thus, for completely damaged pores, $E_{\rm P}$ was determined by the absorption effect of crude oil and the scattering effect of the surface. Although the absorption effect reduced $E_{\rm P}$, the suppression of the scattering effect on absorption increased $E_{\rm p}$, and the scattering effect was the dominant factor [30]. That led to an increase in $E_{\rm P}$ from 0.0053 to 0.0058 V. During the third stage, the $E_{\rm P}$ decreased with the rising severity of damage. An increase in the oil leakage caused a variation $E_{\rm P}$ of THz signal from 0.0058 to 0.0027 V. This downward trend of $E_{\rm P}$ was more evident in the inset at the bottom of Figure 2. As the oil tank was damaged, more oil leakage occurred, the area of oil leakage even exceeded the area of the pores (diameter: 100 µm). The vibrations and rotational transition frequencies of most organic matter and bio-macro-molecules are in the THz range. The THz wave interacts with the organic matter in the oil, resulting in the THz wave signal's attenuation. Based on the data, THz-TDS technology effectively detected the severity of damage and oil leakage at a micron-scale leak point of the oil tank.

In oil-gas storage and transportation, there was more than one leak point on the oil tank. Accurately measuring the number of micron-scale pores has been important for the safety of oil-gas storage and transportation. The THz-TDS test results on oil tanks with a different number of pores are shown in Figure 3(a). Since the focus of this study is the detection of micron-scaled pores and oil leakage, the type of pore selected in this experiment is completely damaged, but the number of pores is increasing.

The TDS were plotted in Figure 3(a), with $E_{\rm P}$ ranging from 0.0074 to 0.0042 V, corresponding to the oil tank with zero to five pores. A difference in the spectra caused by the number of pores on the same oil tank can be observed using TDS. The $E_{\rm PS}$ were extracted from TDS to represent the difference, as shown in Figure 3(b). A substantial decline was shown between the TDS parameters $E_{\rm P}$ and the number of pores, indicating that there was a THz signal loss effect for the pores on the oil tank. Since the organic matter in oil had strong absorption effects and features in the THz range, so the $E_{\rm P}$ value was lower for oil tanks with more pores in the coverage of the spot. When the number of pores is greater than 5 in the spot coverage, a pore group is formed in this area, the leakage degree in this area is close to that of a single seriously damaged pore, and its THz amplitude is also close to that of a seriously damaged pore. Therefore, the number of pores can be determined according to the relationship in Figure 3(b). Consequently, $E_{\rm P}$ is an important parameter to the detection of oil leakage. The THz technique should be promising as a supplementary tool for diagnosing the status of the oil tank with micron-scale pores.

According to previous studies, the complexity of oil shows that the origin, viscosity, and water content of oil will affect oil response to THz wave. A simple model that explains the transmission properties of the THz wave on the oil tank has been established using the polyethylene (PE) plate and water.

There were four types of damage on the PE plate: intact (i), partially damaged (ii), completely damaged (iii), and ser-



Figure 3 (Color online) (a) THz-TDS for the oil tank with various numbers of pores; (b) $E_{\rm P}$ of the TDS for the oil tank with various numbers of pores.

iously damaged (iv), corresponding to the four types of pores on the oil tank, as shown in Figure 4(a). Some water was dripped into the completely damaged pore (iii) and seriously damaged pore (iv).

The state of the PE plate was shown in Figure 4(b). (i) There were neither pores nor water in the intact area. The THz signal loss was dominated by the PE plate's absorption when the THz wave irradiated this region. However, PE material was almost transparent in the THz band, so there was minimal THz signal attenuation. (ii) Because there was no water in the partially damaged pore, there was little absorption on the PE plate. The surface of the damaged PE plate was rough, which resulted in a strong scattering effect. Hence, the scattering played a dominant role in the attenuation of THz waves. (iii) The completely damaged pore was full of water, affected by surface tension, so water did not overflow from the pore, and the surface was flat. When the THz wave was irradiated to this region, the THz wave's absorption and scattering coexisted in this region, and they competed with each other [31,32]. As the content of water increased, there was an increase in water-related absorption effects. However, this will also cause the surface of the PE plate to gradually become flat, so that the scattering effect was suppressed. The scattering effect was the main factor in these two effects. Thus, the suppression of the scattering effect made the THz signal value increase. (iv) A large amount of water overflowed as the PE plate was further damaged, and the water had strong absorption with THz wave. At this time, the absorption effect was the primary factor of THz signal reduction. It can be seen from the model that the absorption and scattering effects co-occurred when the THz wave penetrated the PE plate. Another simulation experiment was performed to investigate the contribution of absorption and scattering to the loss of the THz signal.

In this experiment, since it took a long time to measure the volatilization process of water and oil, in order to protect the equipment, we replaced it with another THz time-domain



Figure 4 (Color online) (a) A PE plate with four types of pores; (b) schematic diagram of the transmission model of THz waves in oil tank.

spectrometer with a more open structure. The signal-to-noise ratio of this equipment was 43 dB, and its laser power was higher than the previous one. The THz-TDS of air was obtained as a reference. The intact PE plate with a length of 30 mm, a width of 30 mm, a thickness of 1 mm was placed on a horizontal table. Then, 0.25 mL of water was dropped vertically on the plate. After the water evaporated, a pore with a diameter of about 0.5 mm was damaged on the PE plate. The THz-TDS of the intact PE plate, the intact PE plate with water, and the PE plate with pore were obtained, as shown in Figure 5.

As shown in Figure 5(a), there was no apparent attenuation of the intact PE plate's peak intensity compared to the TDS of air, which indicated that the intact PE plate was a transparent material in the THz range. Because no pores were present on the plate, the PE plate had no substantial effect on the transmission of a THz wave when the water was dropped on the intact PE plate. It is apparent that little scattering occurred, and absorption of water played a dominant role with the attenuation ΔE_P of 0.00393 V. The PE plate was damaged after the water evaporated, and the surface of the plate was pitted, so the scattering was dominant and there was almost no absorption with the maximum attenuation ΔE_P of 0.01125 V. Therefore, the effect of scattering contributed greater attenuation of THz signal than the impact of absorption.

An experiment was conducted in which water was continuously dropped onto a PE plate with a micron-scale pore to verify the correctness of the model. The THz-TDS was continuously obtained during the increase of water content with results shown in Figure 5(b).

For the initial state (E_P =0.0133 V), the water-free pore on the PE plate was pitted, which led to severe scattering of the THz wave. During the test, more water was dropped into the pore and the intensity of absorption effects increased. The PE plate's surface gradually flattened, and scattering effects decreased. However, scattering contributed more to the THz signal's attenuation than absorption. Therefore, the E_P increased to 0.0138 V during the first stage because of the inhibitory effect of absorption on scattering. During the second stage, as the water content increased, water overflowed and absorption dominated. There was almost no scattering on the PE plate with the minimum E_P of 0.0118 V, which was consistent with analysis of the model.

The experiment was repeated with oil instead of water to ensure that the model was also applicable in oil-gas storage and transportation. The result was shown in Figure 5(c). As shown in Figure 5(c), E_P 's trend was in close agreement with the experimental result. The variation can be divided into two stages based on the changing tendency. Because of the inhibitory effect of absorption on scattering, the E_P increased in the first stage with a value from 0.01685 to 0.01715 V. However, the E_P rapidly decreased with the rising oil content during the second stage. The THz wave mainly interacted with the organic matter in the oil. The vibrations and rotational transitions of most organic matter and bio-macromolecules were addressed in the THz range. The interaction between the THz wave and the organic matter caused the E_P



Figure 5 (Color online) (a) THz-TDS of air, the intact PE plate, the intact PE plate with water, and the PE plate with pore. The $E_{\rm P}$ of PE plate with varying content of (b) water and (c) oil at different times.

to decrease. A conclusion can be drawn that the above model was applicable in oil-gas storage and transportation.

4 Conclusion

In summary, THz-TDS was used to investigate the severity of damage and oil leakage from oil tanks. The $E_{\rm P}$ strongly depended on the oil tank's severity of damage and decreased as the pores expanded from intact pore to partially damaged pore. After that, the oil content increased with pore expansion, resulting in an initial increase of $E_{\rm P}$ followed by a decrease of $E_{\rm P}$. THz-TDS analysis shows that the THz wave's transmission properties on the oil tank with micronscale pore were considered and modeled. The model suggested that the attenuation of $E_{\rm P}$ was because of absorption and scattering, which played a more critical role. Another simulation experiment was performed to prove the correctness of the model. The experimental results showed that the model could thoroughly explain the THz wave's transmission properties on the oil tank with micron-scale pores. These results were crucial for the improvement and development of THz-TDS technology and played an auxiliary role in the field of oil-gas storage and transportation.

This work was supported by the National Natural Science Foundation of China (Grant No. 11804392), and the Science Foundation of China University of Petroleum, Beijing (Grant Nos. ZX20190163, 2462020YXZZ019 and 2462020YXZZ017).

- Licata M, Aspinall M D, Bandala M, et al. Depicting corrosion-born defects in pipelines with combined neutron/γ ray backscatter: A biomimetic approach. Sci Rep, 2020, 10: 1486
- 2 Shuai J, Han K, Xu X. Risk-based inspection for large-scale crude oil tanks. J Loss Prevention Process Industries, 2012, 25: 166–175
- 3 Shi Y, Mu Z X, Cai M L, et al. Advances in motion control of gas pipeline detection robot. Sci China Tech Sci, 2019, 63: 877–878
- 4 Du W, Wan Y, Zhong N, et al. Status quo of soil petroleum contamination and evolution of bioremediation. Pet Sci, 2011, 8: 502– 514
- 5 Shi Y, Mu Z X, Cai M L, et al. Advances in motion control of gas pipeline detection robot. Sci China Tech Sci, 2019, 63: 877–878
- 6 Ziabakhsh-Ganji Z, Nick H M, Donselaar M E, et al. Synergy potential for oil and geothermal energy exploitation. Appl Energy, 2018, 212: 1433–1447
- 7 Sun L, Chen C, Sun Q Q. Experimental and finite element analyses on the corrosion of underground pipelines. Sci China Tech Sci, 2015, 58: 1015–1020
- 8 Guo X L, Yang K L, Guo Y X. Leak detection in pipelines by exclusively frequency domain method. Sci China Tech Sci, 2012, 55: 743–752
- 9 Liu E, Wang X, Zhao W, et al. Analysis and research on pipeline vibration of a natural gas compressor station and vibration reduction measures. Energy Fuels, 2020, 35: 479–492
- 10 Li S X, Yu S R, Zeng H L, et al. Predicting corrosion remaining life of underground pipelines with a mechanically-based probabilistic model.

J Pet Sci Eng, 2009, 65: 162-166

- 11 Wang L K, Xu B, Wang H C, et al. Oil pipeline leak detection system based on acoustic wave technology. Appl Mech Mater, 2012, 220-223: 1628–1632
- 12 Florian K, Boris G, Andrey B. Modeling acoustic response of permeability variation in deepwater wells using spectral method. J Acoust Soc Am, 2009, 125: 2520–2520
- 13 Fan H, Smeulders D. Broadband acoustic wave experiments in borehole configurations. J Acoust Soc Am, 2017, 142: 2724–2725
- 14 Wang F, Lin W, Liu Z, et al. Pipeline leak detection by using timedomain statistical features. IEEE Sens J, 2017, 17: 6431–6442
- 15 Ramirez-Melendez G, Bello-Jimenez M, Pottiez O, et al. Improved all-fiber acousto-optic tunable bandpass filter. IEEE Photon Technol Lett, 2017, 29: 1015–1018
- 16 Zhan H, Wu S, Bao R, et al. Qualitative identification of crude oils from different oil fields using terahertz time-domain spectroscopy. Fuel, 2015, 143: 189–193
- 17 Bassbasi M, Hafid A, Platikanov S, et al. Study of motor oil adulteration by infrared spectroscopy and chemometrics methods. Fuel, 2013, 104: 798–804
- 18 Leng W, Zhan H, Ge L, et al. Rapidly determinating the principal components of natural gas distilled from shale with terahertz spectroscopy. Fuel, 2015, 159: 84–88
- 19 Ryder M R, Van de Voorde B, Civalleri B, et al. Detecting molecular rotational dynamics complementing the low-frequency terahertz vibrations in a zirconium-based metal-organic framework. Phys Rev Lett, 2017, 118: 255502
- 20 Bao R, Qin F, Chen R, et al. Optical detection of oil bearing in reservoir rock: Terahertz spectroscopy investigation. IEEE Access, 2019, 7: 121755
- 21 Zhan H, Chen R, Miao X, et al. Size effect on microparticle detection. IEEE Trans THz Sci Technol, 2018, 8: 477–481
- 22 Feng X, Wu S X, Zhao K, et al. Pattern transitions of oil-water twophase flow with low water content in rectangular horizontal pipes probed by terahertz spectrum. Opt Express, 2015, 23: A1693
- 23 Tao H, Lin J. Enhancing microwave absorption of metals by femtosecond laser induced micro/nano surface structure. Optics Lasers Eng, 2019, 114: 31–36
- 24 Ahi K, Shahbazmohamadi S, Asadizanjani N. Quality control and authentication of packaged integrated circuits using enhanced-spatialresolution terahertz time-domain spectroscopy and imaging. Optics Lasers Eng, 2018, 104: 274–284
- 25 Shen Y C, Taday P F, Pepper M. Elimination of scattering effects in spectral measurement of granulated materials using terahertz pulsed spectroscopy. Appl Phys Lett, 2008, 92: 051103
- 26 Rotter S, Gigan S. Light fields in complex media: Mesoscopic scattering meets wave control. Rev Mod Phys, 2017, 89: 015005
- 27 Savo R, Pierrat R, Najar U, et al. Observation of mean path length invariance in light-scattering media. Science, 2017, 358: 765–768
- 28 Yan C, Pu M, Luo J, et al. Coherent perfect absorption of electromagnetic wave in subwavelength structures. Optics Laser Tech, 2018, 101: 499–506
- 29 Liu H, Ke L. Measuring low-level porosity structures by using a nondestructive terahertz inspection system. Optics Laser Tech, 2017, 94: 240–243
- 30 Zhan H, Chen M, Zhao K, et al. The mechanism of the terahertz spectroscopy for oil shale detection. Energy, 2018, 161: 46–51
- 31 Bandyopadhyay A, Sengupta A, Barat R B, et al. Effects of scattering on THz spectra of granular solids. Int J Infrared Milli Waves, 2007, 28: 969–978
- 32 Oh G H, Kim H S, Park D W, et al. *In-situ* monitoring of moisture diffusion process for wood with terahertz time-domain spectroscopy. Optics Lasers Eng, 2020, 128: 106036