

Enhancement and mechanism of tourmaline on activating water by high-voltage pulsed discharge pre-treatment

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ABSTRACT

Due to the characteristic of far-infrared radiation and spontaneous polarization, the tourmaline is used for activating water by reducing the water clusters. In this study, an innovative approach of high-voltage pulse discharge (HVPD) pre-treatment is first proposed to enhance the performance of tourmaline activating water. The results indicate the performance of far-infrared radiation and releasing anion are strengthened distinctly via the HVPD pre-treatment. With the increase of pulse numbers and the decrease of particle size, the full width at half maxima of ^{17}O in the nuclear magnetic resonance line reduces, indicating the decrease of water clusters size. Owing to the HVPD pre-treatment, the surface tension of water decreases, and the conductivity and dissolved oxygen of water increases. The scanning electron microscopy analysis shows the micro-cracks generate in the surface of tourmaline after pre-treatment; meanwhile, the performance of far-infrared radiation is enhanced, and thus the activation degree of water is improved.

Keywords: High-voltage pulse discharge; Tourmaline; Water clusters; Nuclear magnetic resonance; Far-infrared radiation

1. Introduction

Generally, the clusters exist in water instead of the single-molecule H_2O [1]. Compared with the macromolecular cluster, the higher performance of solubility, permeability, dissolved oxygen capacity, and lower surface tension are presented in the small-molecular cluster [2]. It is significant to reduce the size of water clusters on account of the stronger activity of small-molecular water. The water clusters are connected mainly depending on the hydrogen bonds between molecules. Hence, destroying the hydrogen bond is the primary approach to reduce the water cluster. The conventional methods of activating water include external magnetic-field, external electric-field, far-infrared

radiation, direct-heating, and microwave [3,4], whereas additional energy is required in these methods. As a kind of healthy and environmentally minerals materials, the tourmaline has the excellent performance of far-infrared radiation and the dipole moment characteristic [5,6]. Due to the molecular thermal motion, the dipole moment will transform. In other words, the thermal motion promotes the polar molecule stimulated to the higher energy level. The redundant energy is released as an electromagnetic wave in the transition process. The tourmaline radiates the far-infrared rays with a wavelength of 4–18 μm [7,8].

The high-voltage pulse discharge (HVPD) pre-treatment is an innovative technology for solid materials breakage, which has been gradually applied to oil exploitation,

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medical, and chemical-fields [9–11]. In recent years, with the development of HVPD technology, it has been widely used in the blasting of national defense and military. Because the breakdown strength of ores is less than deionized water at the voltage rise time less than 500 ns, the ores are first broken down [12–14]. Based on the different properties of dielectric and conductivity between metallic minerals and gangue, the plasma channel develops along with the mineral interface easily [15]. Besides, the plasma explosion and thermal expansion stress generate at the mineral interface (Fig. 1).

Meanwhile, the shock waves and destructive forces fields promote the generation and propagation of cracks [16], which ultimately bring about the macroscopic fracture of the ore. The plasma channel expands and explodes rapidly in consideration of the high-temperature and high-pressure environment generated by pulse discharge [17,18]. The shock wave promotes primary-crack growth and secondary-crack initiation [19,20]. The density of micro-cracks in the ore significantly improves, and the mechanical strength of the ore is weakened [21]. A large number of active sites and exposed hydroxyl are presented due to the micro-cracks of tourmaline, and the performance of radiating far-infrared rays and releasing negative ions is enhanced. Moreover, the spontaneous polarization effect of tourmaline is strengthened.

In the present study, an innovative HVPD pre-treatment technology is proposed to enhance the performance of tourmaline activating water. The particle size and pulse number are ascertained by the surface tension, dissolved oxygen, and conductivity of water. The size of water clusters is ascertained by the full width at half maxima (FWHM) of ^{17}O in the nuclear magnetic resonance (NMR). The performance of tourmaline releasing negative ion and radiating far-infrared are studied to reveal the mechanism of destroying hydrogen bonds. The microscopic structure and hydrogen bond strength are characterized by scanning electron microscopy (SEM) and Fourier-transform infrared spectroscopy (FTIR).

2. Materials and methods

2.1. Raw materials

Typical tourmaline collected from Chifeng, Inner Mongolia, China is the core samples in this experiment, which were purified by a combination process of low-intensity magnetic separation and high-intensity magnetic separation. The chemical composition analysis result of tourmaline is exhibited in Table 1, which consists of 9.10% B_2O_3 , 34.88% SiO_2 , and 22.77% Al_2O_3 . Fig. 2 shows the X-ray diffraction pattern of the sample where tourmaline is found to be high purity and well-developed crystalline form.

2.2. HVPD pre-treatment

The HVPD apparatus was designed by scholars from Northeastern University and Shenyang Ligong University, which consists of a pulsed high-voltage power supplier, a breakage cavity, and a needle-to-plate electrode. The output voltage and electrode spacing were 15–30 kV and 1 mm. In the HVPD experiment, the tourmaline powder was placed in the discharge chamber with the deionized water as an insulating liquid. The counter recorded the pulse numbers and the single-phase voltage regulator adjusted the appropriate voltage for the experiment (Fig. 3). The pre-treated tourmaline powder and 100 mL deionized water were placed in a 250 mL beaker, stirring with a magnetic stirrer for 10 min at 17°C. The supernatant was centrifugalized from activation water to detect the different properties of water.

2.3. Analysis methods

The JK99C automatic surface tension meter (Shanghai, China) was used to detect the surface tension of water in this paper. The test equipment of dissolved oxygen was Multi 3510 IDS portable dissolved oxygen meter (Munich, Germany). The DDS-304 electric conductivity meter

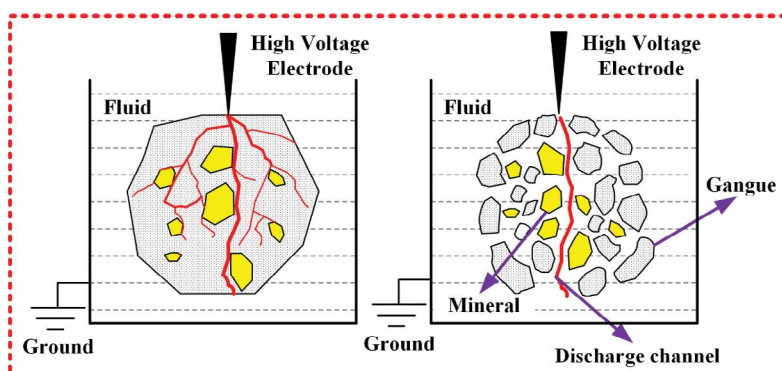


Fig. 1. Diagram of high-voltage pulse discharge breakage.

Table 1
Chemical composition (mass fraction, %) of tourmaline sample

Composition	B_2O_3	SiO_2	Al_2O_3	TFe	MgO	CaO	Na	TiO_2
Content	9.10	34.88	22.77	13.77	4.28	1.56	1.31	0.92

(Shanghai, China) was the test equipment to analyze the conductivity of water. The width of the spectral line usually expresses as the FWHM. The NMR is extensively used to study the association of water molecules. The size of liquid water clusters was characterized by the FWHM of ^{17}O using the 500 M NMR spectrometer (Shanghai, China) in this paper. The surface microstructure and specific surface area of tourmaline were characterized by SEM (SSX-550, Japan). The number of anions released was detected by the DLY-4 (Zhangzhou, China) air ion measuring instrument. The IR-2 double-band emissivity meter (Shanghai, China) was used to inspect the far-infrared ray radiated by tourmaline in

this experiment. The infrared spectrum of water activated by pre-treated tourmaline was determined by Nicolet 380 FTIR spectrometer (Thermo, USA) in this study.

3. Results and discussion

3.1. Effects of HVPD factors on the performance of tourmaline on activating water

3.1.1. Effects of pulse number on the performance of tourmaline

The effect of pulse number on the performance of tourmaline on activating water was investigated with the pulse number varying from 30 to 150, the particle size $0.79\ \mu\text{m}$, the output voltage 15 kV, a tourmaline dosage of 20 g/L (Fig. 4). A clear trend is shown in Fig. 4 that the surface tension declined with the pulse number, indicating that the better performance of tourmaline on activating water was obtained at more pulse numbers. The surface tension of water activated by the pre-treated tourmaline decreased from 72.17 to 71.82 mN/m gradually as the pulse numbers varying from 30 to 150.

Given the perspective of intermolecular interaction, the surface tension of liquid generates due to the asymmetric force field of the surface molecules. The hydrogen bond is the strongest force among water molecules, which causes that the surface tension of water was higher than the liquid connected by Van der Waals force. The water clusters generate depending on the hydrogen bond in the intermolecular of water, which increases the water association degree. The far-infrared radiation generated by tourmaline destroys the hydrogen bonds between water molecules

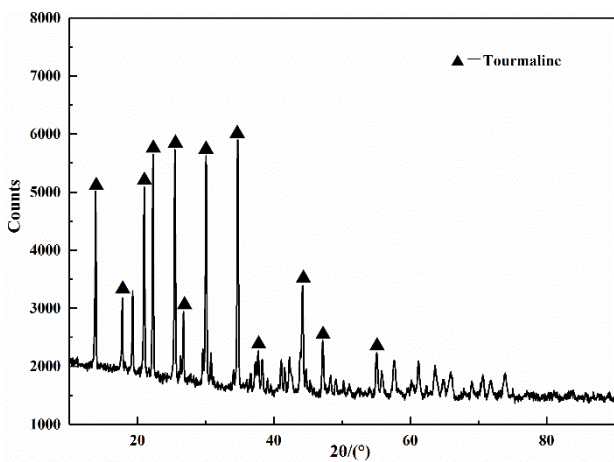


Fig. 2. The tourmaline pattern was examined by X-ray diffraction.

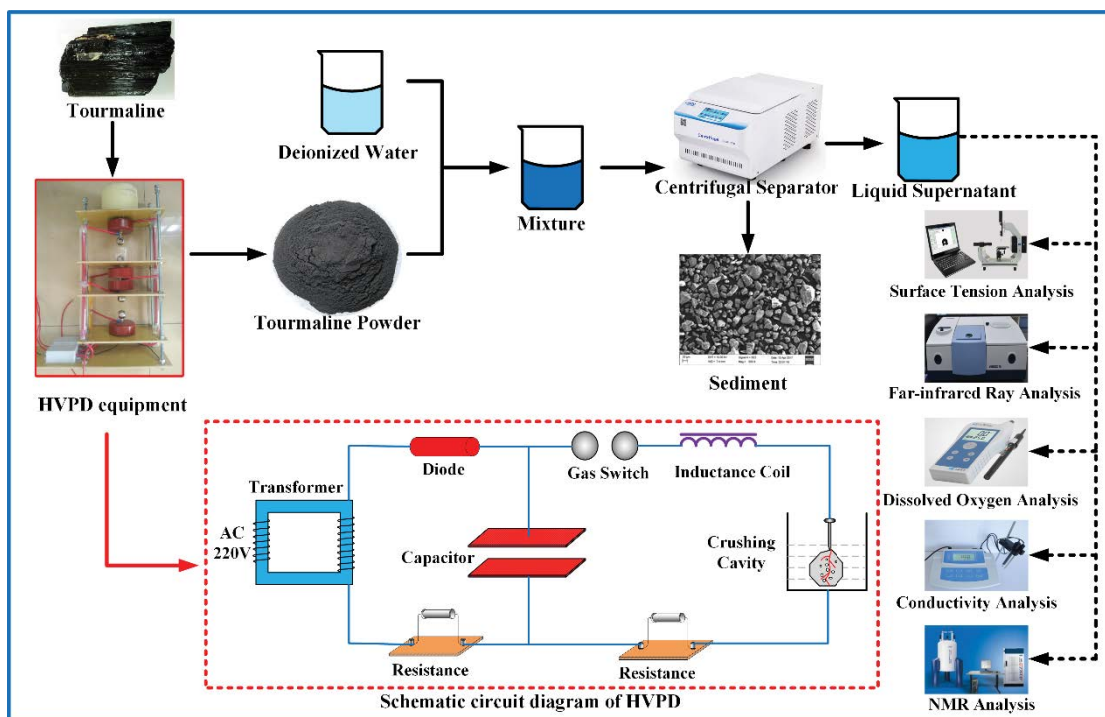


Fig. 3. The procedure for pretreatment and activating water tests of tourmaline samples.

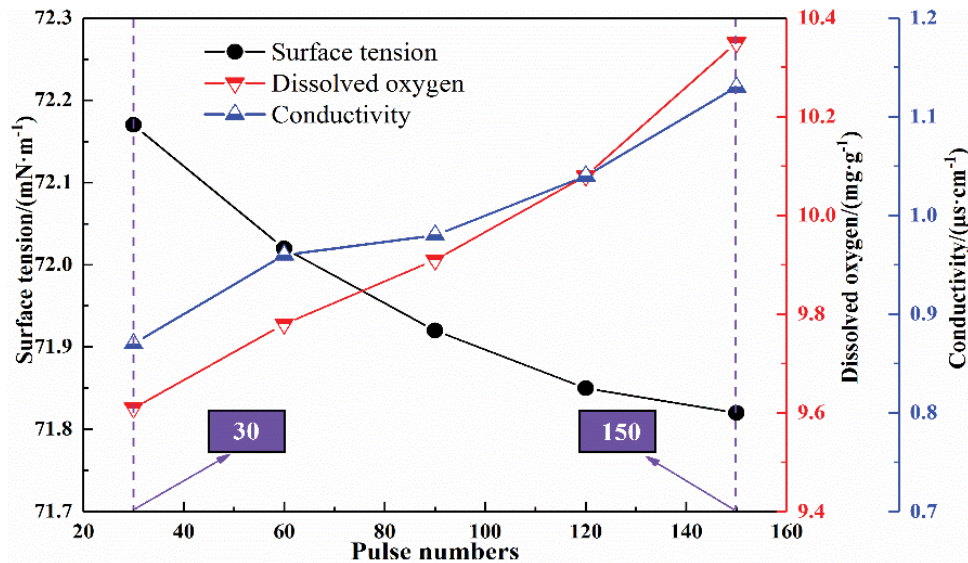


Fig. 4. Effect of pulse number on surface tension, dissolved oxygen, and conductivity.

effectively. Meanwhile, the water molecule clusters size and the surface tension reduce [22–26]. The performance of tourmaline radiating far-infrared was enhanced by the HVPD pre-treatment. Hence, the effect of tourmaline reducing the surface tension of water would be strengthened by HVPD pre-treatment.

The dissolved oxygen and conductivity of water activated by the pre-treated tourmaline gradually increased with pulse number. At pulse number 150, the dissolved oxygen and conductivity of the activated water reached to 10.35 mg/g and 1.13 $\mu\text{s}/\text{cm}$, respectively. At pulse number 30, the minimum dissolved oxygen and conductivity of the pre-treatment tourmaline activated water was 9.61 mg/g and 0.87 $\mu\text{s}/\text{cm}$ respectively, which were higher than the activated water by untreated tourmaline of 9.57 mg/g and 0.53 $\mu\text{s}/\text{cm}$. It was concluded that the performance of tourmaline on activating water was enhanced by the HVPD pre-treatment, where the surface tension declined, dissolved oxygen, and conductivity increased distinctly.

The intermolecular hydrogen bond of water was destroyed by the far-infrared radiation of tourmaline, and the water clusters size reduced. The adsorption centers of oxygen molecules in water increased gradually, and this promoted the oxygen molecules dissolved in water more easily. Therefore, the dissolved oxygen of water increased. Due to the destruction of the hydrogen bond between water molecules, the ionization degree of water increased and the association degree decreased [8]. The movement speed of charged particles and the conductivity increased. The performance of tourmaline radiating far-infrared was enhanced by the HVPD pre-treatment. Hence, the dissolved oxygen and conductivity of water would be improved by the pre-treated tourmaline.

3.1.2. Effects of particle sizes on the performance of tourmaline

The activated water experiments were performed at particle size 0.79, 1.8, 13.6, 25.6, and 44.6 μm , output voltage

15 kV, pulse number 100, tourmaline dosage 20 g/L. The influence of particle size on the surface tension, dissolved oxygen, and conductivity of activated water is shown in Fig. 5. Fig. 5 indicates that with the increase of tourmaline particle size, the surface tension gradually increased, which was enlarged by 0.27 mN/m as the particle size increased from 0.79 to 44.6 μm . A clear trend was observed that the dissolved oxygen decreased with the increase in tourmaline particle size, with a variation of 0.81 mg/g between 0.79 and 44.6 μm . A similar trend showed that the conductivity decreased with the increase in tourmaline particle size, with a variation of 0.42 $\mu\text{s}/\text{cm}$ between 0.79 and 44.6 μm . Better performance of pre-treated tourmaline activating water appeared at the smaller tourmaline particle size.

Because of the spontaneous polarization effect, the electric-field intensity of 10^4 – 10^7 V/m generated on the surface of tourmaline [3]. The water molecules were ionized to produce H^+ and OH^- in the electric-field. Ultimately, the active molecules H_3O^+ and H_2O_2 generated owing to the combination of H^+ , OH^- , and H_2O , resulting in a strong interfacial activity of water molecules [3,8]. Besides, the cluster structure of water molecules was influenced by the electric field. As a kind of polar molecule, the electric dipole interaction of water is the primary cause of the formation of an intermolecular hydrogen bond. The hydrogen-bonding network system of water clusters was transformed by the external electric field. The macromolecular clusters water was disintegrated into micro molecule water through weakening and cutting off the hydrogen bond between water molecules, which promoted the activation of water effective [27–29]. Due to the stronger effect of the electric-field, the hydrogen bond was weakened more significantly at the smaller particle size. The weakening of hydrogen bond resulted in the decrease of water molecular cluster size and surface tension, and the increase of dissolved oxygen [30,31]. The HVPD pre-treatment enhanced the performance of tourmaline destroying the hydrogen bonds. Hence, the dissolved oxygen and conductivity of water were improved.

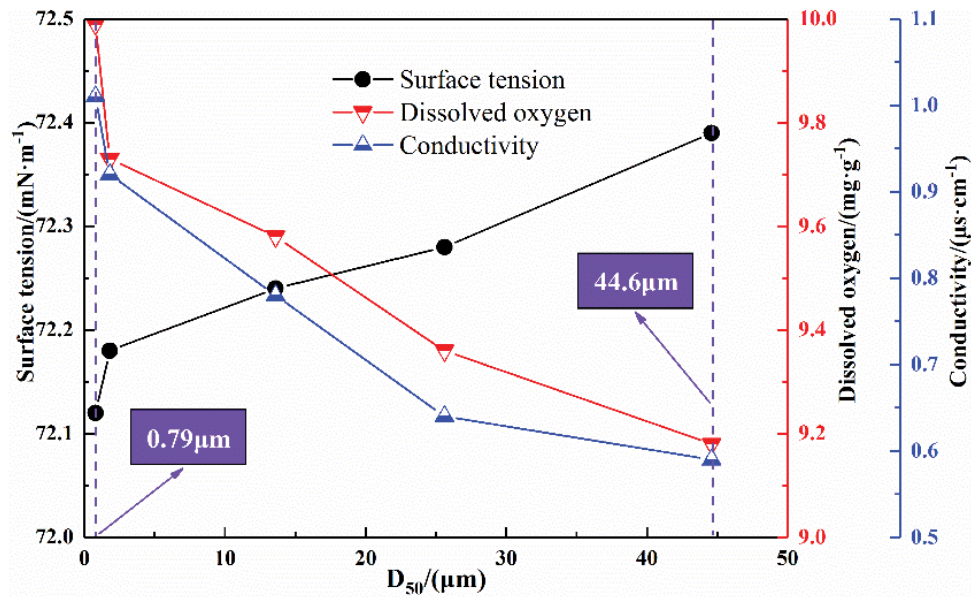


Fig. 5. Effect of particle size on surface tension, dissolved oxygen, and conductivity.

3.2. Performance of tourmaline negative ion released and far-infrared radiation

The experiments of tourmaline releasing negative ion were performed at output voltage 30 kV and pulse number 100. From Fig. 6 it is observed that with the extension of particle size, the amount of negative ion firstly increased and then decreased. The maximum amount of negative ion appeared at particle size 1.8 μm , with the numbers of negative ion in untreated and pretreated tourmaline were 1,023 and 1,175 cm^{-3} , respectively. Meanwhile, compared with the untreated tourmaline, the negative ion amount of pretreated samples presented a significant improvement, indicating that the performance of releasing negative ion was enhanced by the HVPD pre-treatment distinctly.

Due to the permanent spontaneous electrode of tourmaline and surface electric-field energy of 25 eV, the water

molecule (ionization energy 1.25 eV) was easily ionized to form H^+ and OH^- [4,6]. The ion equations were exhibited as follow:



The H_3O_2^- is a basic anion, which is known as the air negative ion. The smaller particle size of tourmaline had a larger surface area and a higher surface activity. The increase of the contact area of water and tourmaline promoted the ionization of the water molecule. On the other hand, the

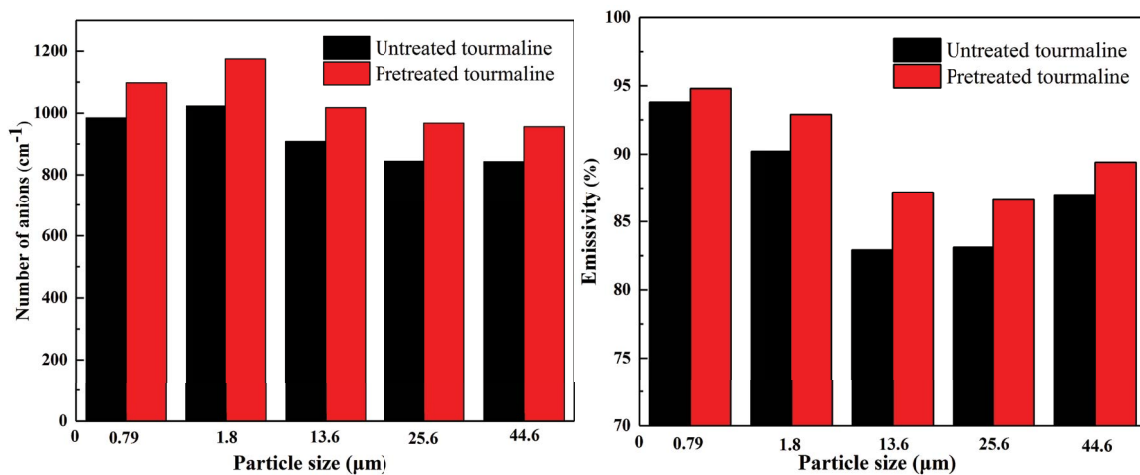


Fig. 6. Effect of HVPD on tourmaline releasing negative ion and radiating far-infrared rays.

number of negative ions increased due to the stronger electric-field intensity. However, the internal structure defects of tourmaline sizes increased as the long grinding time, which weakened the performance of spontaneous polarization. Therefore, the negative ion number at 0.79 μm was less than the number at 1.8 μm . Moreover, the micro-crack generated in the HVPD pre-treatment enhanced the performance of spontaneous polarization. Hence, the number of negative ion of tourmaline increased via the HVPD pre-treatment.

The experiments of tourmaline radiating far-infrared were carried out at output voltage 30 kV and pulse number 100. Fig. 6 indicates that with the increase in particle size, the emissivity firstly decreased and then increased. The minimum emissivity was appeared at particle size 13.6 μm , with the emissivity of untreated and pretreated tourmaline were 82.9% and 87.2%, respectively. The enlargement of emissivity was 1.2, 4.3, and 2.5 percentage points at a particle size of 0.79, 13.6, 44.6 μm , respectively. It was concluded that the performance of radiating far-infrared rays was enhanced by the HVPD pre-treatment observably.

Due to the spontaneous polarization effect of tourmaline, the spontaneous electric field generates to break the hydrogen bond of water. Moreover, the radiating far-infrared rays of tourmaline increase the water temperature, and the hydrogen bond has been destroyed due to the change of temperature. The HVPD pre-treatment improved the performance of spontaneous polarization effect and radiating far-infrared rays, thus the water has been activated by the pretreated tourmaline.

The decrease in tourmaline particle size increased the surface free energy and the ratio of polar composition, and the performance of far-infrared emission was improved. The superficial area increased with the decrease of particle size. Compared with the large particle, the surface energy and surface activity increased obviously, which were conducive to promote the particle transiting from the “ground state” (the lowest energy level) to the “excited state” of (the higher energy level) by absorbing the additional energy [6,7]. Therefore, theoretically, the better performance of radiating far-infrared was obtained at the smaller particle size. Due to the resonance between the hydrogen bond of water molecules and the far-infrared ray emitted by

tourmaline, the hydrogen bonds were broken to decrease the water cluster size. The performance of surface activity was enhanced due to the micro-crack generated by the HVPD. Hence, the performance of tourmaline radiating far-infrared was improved via the HVPD pre-treatment.

3.3. Effects of HVPD parameters on the FWHM of the NMR line

3.3.1. Effect of particle size on the FWHM of NMR line

Generally, the clusters exist in water instead of the single-molecule H_2O . However, the water clusters are not stable. The dynamic equilibrium of water molecule's divorce and combine with the water clusters exist in the system. Therefore, the water clusters size is an average value, which will be transformed with the environment status. The NMR is a conventional technology to ascertain the water clusters size.

The effect of tourmaline particle size on the performance of water clusters was studied by using NMR, with the particle size of 0.79, 1.8, 13.6, 25.6, and 44.6 μm , output voltage 30 kV, the pulse number at 100, a tourmaline dosage of 20 g/L (Fig. 7). As shown in Fig. 7, the FWHM of the NMR line increased with tourmaline particle size. With the particle size varying from 0.79 to 44.6 μm , the FWHM of the NMR line enlarged from 591 to 1,003 Hz, indicating that the water clusters increased and the activity of water declined with particle size.

The optimal activation effect appeared at particle size 0.79 μm , which showed that the better performance of reducing water clusters was obtained at the smaller particle size of tourmaline powder. Besides, the FWHM minimum 591 Hz was less than FWHM of untreated tourmaline activating water (766 Hz), indicating that the performance of tourmaline reducing water clusters was strengthened via the HVPD pre-treatment. Accordingly, the activation performance of water had been enhanced significantly via tourmaline pretreated by the HVPD.

The transformation of the water cluster structure depended on the hydrogen bond between the water molecules. The surface electric-field of tourmaline heightened with the decrease of particle size to result in strong destruction of

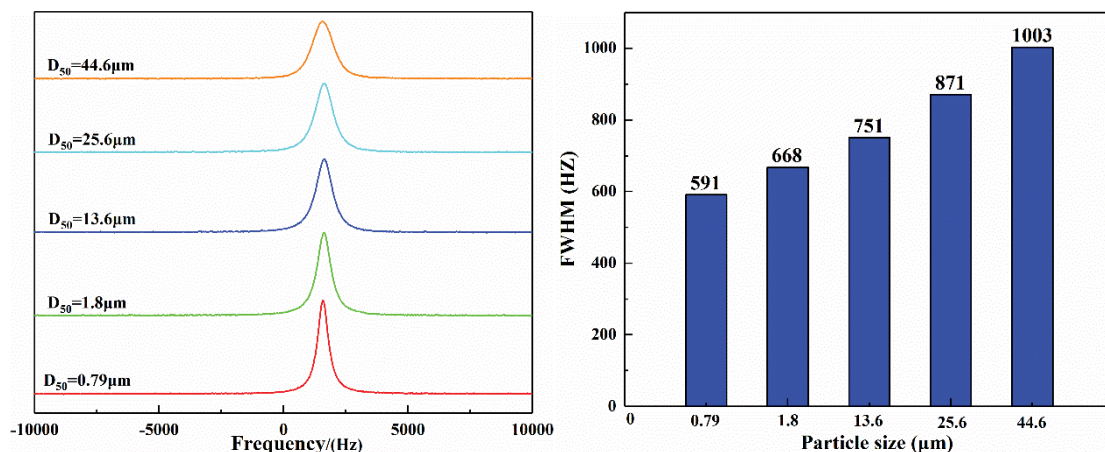


Fig. 7. Effect of particle size on FWHM of ^{17}O NMR line.

hydrogen bond [32,33]. Meanwhile, the association degree of water molecules and the FWHM of the NMR line reduced. The HVPD pre-treatment enhanced the performance of tourmaline radiating far-infrared. Hence, the effect of tourmaline reducing the water clusters sizes would be enhanced by the HVPD pre-treatment.

3.3.2. Effect of pulse number on the FWHM of NMR line

The influence of pulse number on the performance of tourmaline reducing water clusters was investigated by using NMR, with the pulse number varying from 30 to 150, the particle size at 0.79 μm , output voltage 30 kV, a tourmaline dosage of 20 g/L (Fig. 8). A clear trend showed that the FWHM of the NMR line declined with the pulse number. The FWHM was 464 and 703 Hz at the pulse number 150 and 30, indicating the lower association degree of water was obtained at more pulse number and longer discharge time. Besides, the FWHM maximum 703 Hz was less than FWHM of untreated tourmaline activating water (766 Hz), indicating that the performance of tourmaline reducing water clusters was strengthened via the HVPD pre-treatment.

The surface crack of tourmaline increased with the addition of pulse numbers. Hence, the surface activity and electric-field intensity increased, and lots of broken bonds and surface hydroxyl were produced. The performance of destroying the hydrogen bonds was strengthened. Meanwhile, the HVPD pre-treatment reduced the water clusters sizes, and the FWHM of the NMR line decreased as the augment of pulse numbers. It was concluded that the HVPD pre-treatment promoted the performance of tourmaline activating the water molecular.

3.4. Analysis of morphology surface characteristics and hydrogen bond strength

3.4.1. Morphology structure characterization

The SEM analysis was used to investigate the microstructure of tourmaline by the HVPD pre-treatment. Fig. 9 shows several cracks of different sizes generated in the

tourmaline assisted by the HVPD pre-treatment. When the electric pulses were exerted on the tourmaline powder, the breakdown occurred inside and resulted in the discharge channel. Extremely high energy was accumulated in the discharge channel for a very short time, resulting in the rapid rise of discharge channel temperature. Meanwhile, extreme pressure generated in the discharge channel, thus the originally narrow discharge channel was expanded rapidly [9–12]. A strong pressure wave generated inside of the tourmaline powder around the discharge channel, causing the tourmaline particles bursting or even disintegrating [17,19,20]. Therefore, the cracks appeared on the surface of tourmaline powder, and the specific surface area also increased [18–21]. Thus the HVPD pre-treatment enhanced the performance of releasing negative ions and radiating far-infrared rays. The interaction area of water and tourmaline increased through the cracks, which indicated that tourmaline samples interacted with water effectively, and the activity of water was enhanced.

Due to the chemical bond breakage, a large number of hydroxyl and positive ion appeared on the tourmaline surface, and the surface-active site and electric-field intensity were improved. The cracks number of the HVPD pre-treatment products was larger than the untreated samples, where many broken-bond and hydroxyl appeared [22,23]. The surface hydroxyl and metal positive ion were attracted by the water molecules easily to produce the negative electricity on the tourmaline surface. Because of the electron and positive ion (Mg^{2+} , Ca^{2+} , Fe^{2+} , Al^{3+} , Na^+ , K^+ , and B^{3+}), the electron transfer was enhanced to improve the conductivity of water.

3.4.2. Hydrogen bond strength

FTIR analysis was performed to analyze the strength of hydrogen bonds in tourmaline activating water. Fig. 10 shows that the strong absorption capacity of infrared radiation appeared near the frequency of 3,200 and 1,600 cm^{-1} . After the HVPD pre-treatment of tourmaline, the absorption peak of the O-H bond in activated water moved from 3,459.79 to 3,460.84 cm^{-1} , indicating the

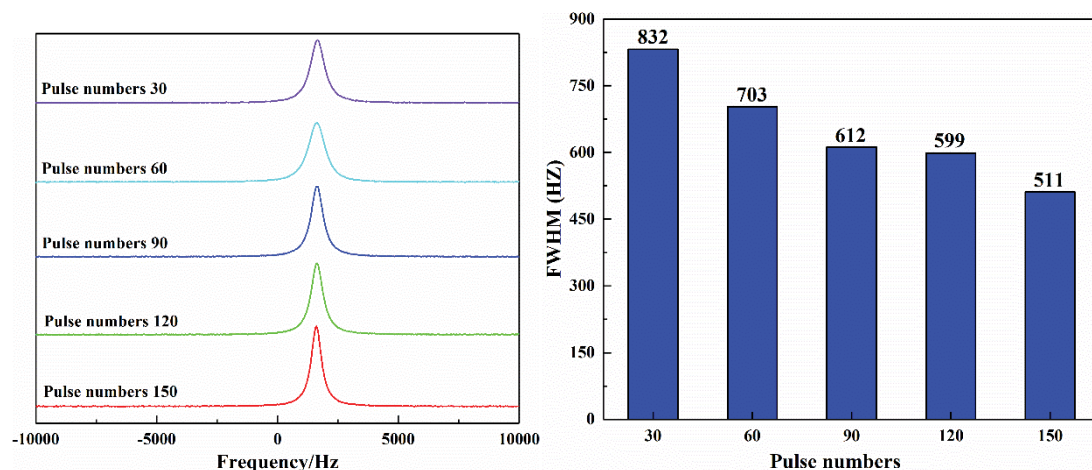


Fig. 8. Effect of pulse numbers on FWHM of ^{17}O NMR line.

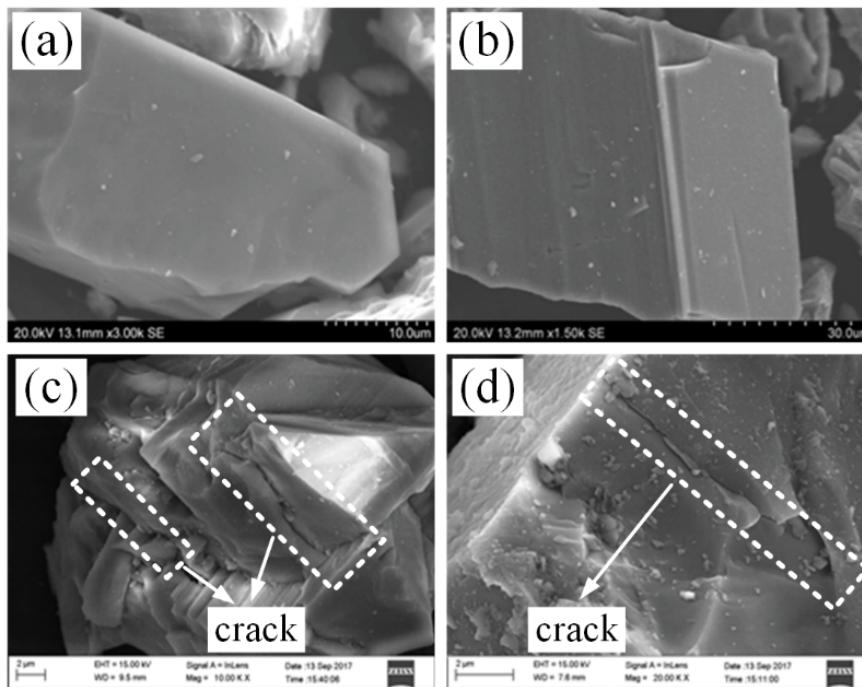


Fig. 9. Apparent morphology of pretreated and untreated tourmaline sample. (a, b) untreated sample and (c, d) pretreated sample.

weaker hydrogen bond of water. In other words, the HVPD pre-treatment enhanced the activation characteristics of water.

In consideration of the micro-crack in the surface of pretreated tourmaline, the surface energy increased via the HVPD pre-treatment, resulting in a better performance of spontaneous polarization. Meanwhile, the performance of releasing anion and radiating far-infrared ray was strengthened, which was conducive to destroy the hydrogen bond and reduce the sizes of water clusters (Fig. 11).

4. Conclusions

- The HVPD pre-treatment was proposed to enhance the performance of tourmaline activating water. The results showed that the surface tension declined, dissolved oxygen, and conductivity increased as the increase of pulse number and the decrease in particle size. The optimum indicators of surface tension 71.82 mN/m, dissolved oxygen 10.53 mg/g, and conductivity 1.13 $\mu\text{s}/\text{cm}$ were obtained at pulse number 150 and particle size 0.79 μm .
- The HVPD pre-treatment enhanced the performances of tourmaline releasing anion and radiating far-infrared rays, which was conducive to break the hydrogen bond of water and reduce the water clusters sizes. The results showed that the FWHM of the NMR line declined with the increase of pulse number and the decrease of particle size, indicating that the water clusters sizes were reduced.
- The results of microstructure analysis showed the HVPD pre-treatment produced micro-cracks on the tourmaline surface, which increased the surface active site and surface area. Meanwhile, the HVPD pre-treatment was

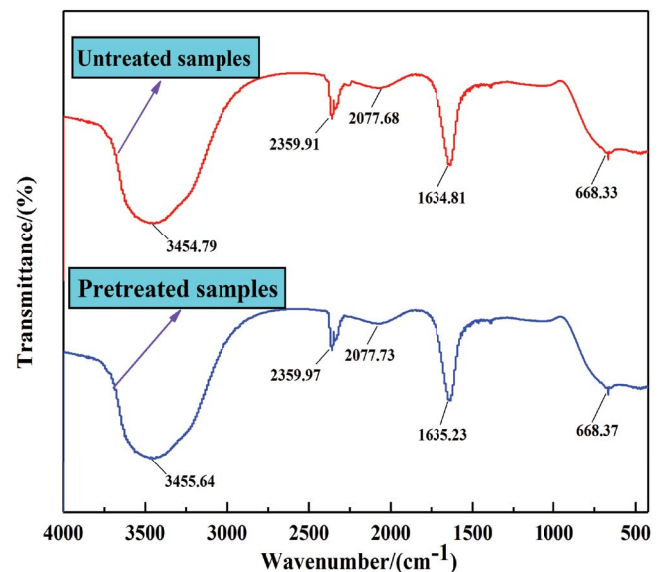


Fig. 10. Infrared spectra results of water activated by tourmaline before and after pretreatment.

conductive to improve the performance of tourmaline radiating far-infrared and tourmaline activating water.

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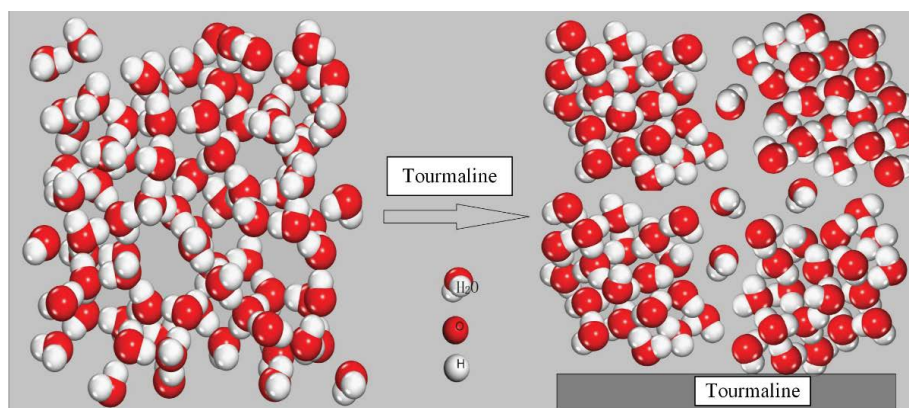


Fig. 11. Structure models of water clusters activated by tourmaline.

References

- [1] D.-S. Ahn, I.-S. Jeon, S.-H. Jang, S.-W. Park, S.-Y. Lee, W.-J. Cheong, Hydrogen bonding in aromatic alcohol-water clusters: a brief review, *Bull. Korean Chem. Soc.*, 24 (2003) 695–702.
- [2] J.S. Liang, D.B. Zhu, J.P. Meng, L.J. Wang, F.P. Li, Z.G. Liu, Y. Ding, L.H. Liu, G.C. Liang, Performance and application of far infrared rays emitted from rare earth mineral composite materials, *J. Nanosci. Nanotechnol.*, 8 (2008) 1203–1210.
- [3] J.P. Meng, J. Liu, X.L. Huo, J. Li, Conductivity method of alkaline solution in evaluating the spontaneous polarization property of tourmaline, *Appl. Mech. Mater.*, 320 (2013) 584–589.
- [4] X. Gai, Effect of Rare Earth Complex on Negative Oxygen Ion Release and Infrared Radiation Characteristics of Tourmaline, China University of Geosciences, Beijing, 2018.
- [5] R.H. Li, Z.P. Jiang, H.W. Yang, Y.T. Guan, Effects of ions in natural water on the ^{17}O NMR chemical shift of water and their relationship to water cluster, *J. Mol. Liq.*, 126 (2006) 14–18.
- [6] Y. Yan, X.-X. Ou, H.-P. Zhang, Y. Shao, Effects of nano-materials on ^{17}O NMR line-width of water clusters, *J. Mol. Struct.*, 1051 (2013) 211–214.
- [7] J.P. Meng, X.L. Huo, J. Liu, Y.F. Pan, Influence of tourmaline mineral material on structure and physical and chemical properties of water, *Appl. Mech. Mater.*, 320 (2013) 577–583.
- [8] D.B. Zhu, J.S. Liang, Y. Ding, G. Xue, L.H. Liu, Effect of heat treatment on far infrared emission properties of tourmaline powders modified with a rare earth, *J. Am. Ceram. Soc.*, 91 (2008) 2588–2592.
- [9] T. Nakamura, T. Kubo, Tourmaline group crystals reaction with water, *Ferroelectrics*, 137 (1992) 13–31.
- [10] E. Wang, F.N. Shi, E. Manlapig, Factors affecting electrical comminution performance, *Miner. Eng.*, 34 (2012) 48–54.
- [11] E. Wang, F.N. Shi, E. Manlapig, Pre-weakening of mineral ores by high voltage pulses, *Miner. Eng.*, 24 (2011) 455–462.
- [12] U. Andres, Development and prospects of mineral liberation by electrical pulses, *Int. J. Miner. Process.*, 97 (2010) 31–38.
- [13] U. Andres, Dielectric separation of minerals, *J. Electrostat.*, 37 (1996) 227–248.
- [14] U. Andres, Electrical disintegration of rock, *Miner. Process. Extr. Metall. Rev.*, 14 (1995) 87–110.
- [15] F.N. Shi, E. Manlapig, W.R. Zuo, Progress and challenges in electrical comminution by high-voltage pulses, *Chem. Eng. Technol.*, 37 (2014) 765–769.
- [16] S.H. Cho, M. Yokota, M. Ito, S. Kawasaki, S.B. Jeong, B.K. Kim, K. Kaneko, Electrical disintegration and micro-focus X-ray CT observations of cement paste samples with dispersed mineral particles, *Miner. Eng.*, 57 (2014) 79–85.
- [17] F.N. Shi, W.R. Zuo, E. Manlapig, Characterisation of pre-weakening effect on ores by high voltage electrical pulses based on single-particle tests, *Miner. Eng.*, 50–51 (2013) 69–76.
- [18] W.R. Zuo, F.N. Shi, E. Manlapig, Modelling of high voltage pulse breakage of ores, *Miner. Eng.*, 83 (2015) 168–74.
- [19] U. Andres, Parameters of disintegration of rock by electrical pulses, *Powder Technol.*, 58 (1989) 265–269.
- [20] G.H. Yan, B. Zhang, B. Lv, G.Q. Zhu, X.N. Zhu, Y.M. Zhao, Enrichment of chalcopyrite using high-voltage pulse discharge, *Powder Technol.*, 340 (2018) 420–427.
- [21] F.Z. Yan, B.Q. Lin, J. Xu, Y.H. Wang, X.L. Zhang, S.J. Peng, Structural evolution characteristics of middle-high rank coal samples subjected to high-voltage electrical pulse, *Energy Fuels*, 32 (2018) 3263–3271.
- [22] P. Gao, S. Yuan, Y.X. Han, Y.J. Li, H.Y. Chen, Experimental study on the effect of pretreatment with high-voltage electrical pulses on mineral liberation and separation of magnetite ore, *Minerals*, 7 (2017) 153, doi: 10.3390/min7090153.
- [23] V.A. Chanturiya, I.Zh. Bunin, M. Ryazantseva, XPS study of sulfide minerals surface oxidation under high-voltage nanosecond pulses, *Miner. Eng.*, 143 (2019) 105939.
- [24] T. Parker, F.N. Shi, C. Evans, M. Powell, The effects of electrical comminution on the mineral liberation and surface chemistry of a porphyry copper ore, *Miner. Eng.*, 82 (2015) 101–106.
- [25] A. Zhu, Preparation of Ultra-Fine Product of Tourmaline and its Improvement Effect and Mechanism for Aquaculture, Jiangnan University, Wuxi, 2012.
- [26] Y. Pan, Research of Activating Water and Biological Effects of Tourmaline Mineral Material, Hebei University of Technology, Tianjin, 2006.
- [27] J.-T. Yeh, W. Wei, H.-H. Hsiung, T. Jiang, Negative air ions releasing properties of tourmaline contained ethylene propylene diene terpolymer/polypropylene thermoplastic elastomers, *J. Appl. Polym. Sci.*, 109 (2008) 82–89.
- [28] S. Sun, C.D. Wei, Y.X. Liu, Characterization and water activation behavior of tourmaline nanoparticles, *J. Nanosci. Nanotechnol.*, 10 (2010) 2119–2124.
- [29] L.D. Tijing, M.-H. Yu, C.-H. Kim, A. Amarjargal, Y.C. Lee, D.-H. Lee, D.-W. Kim, C.S. Kim, Mitigation of scaling in heat exchangers by physical water treatment using zinc and tourmaline, *Appl. Therm. Eng.*, 31 (2011) 2025–2031.
- [30] D.B. Chesnut, Structures, energies, and NMR shieldings of some small water clusters on the counterpoise corrected potential energy surface, *J. Phys. Chem. A*, 106 (2002) 6876–6879.
- [31] K. Kristinaitytė, L. Dagys, J. Kausteklis, V. Klimavicius, I. Doroshenko, V. Pogorelov, N.R. Valevičienė, V. Balevicius, NMR and FTIR studies of clustering of water molecules: from low-temperature matrices to nano-structured materials used in innovative medicine, *J. Mol. Liq.*, 235 (2017) 1–6.
- [32] C. Lao-ngam, M. Phonyiem, S. Chaiwongwattana, Y. Kawazoe, K. Sagarik, Characteristic NMR spectra of proton transfer in protonated water clusters, *Chem. Phys.*, 420 (2013) 50–61.
- [33] J.P. Meng, W. Jin, J.S. Liang, Y. Ding, K. Gan, Y.D. Yuan, Effects of particle size on far infrared emission properties of tourmaline superfine powders, *J. Nanosci. Nanotechnol.*, 10 (2010) 2083–2087.