

Research Article

Solidification and Stabilization of Spent TBP/OK Organic Liquids in a Phosphate Acid-Based Geopolymer

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A method for solidifying spent tributyl phosphate and kerosene (TBP/OK) organic liquids in a phosphate acid-based geopolymer (PAG) was investigated. The TBP/OK emulsion containing tween 80 (T80), TBP/OK organic liquids, and H_3PO_4 was prepared. The TBP/OK emulsion was mixed with metakaolin to obtain solidified TBP/OK forms (SPT). The compressive strength of the SPT was up to 59.19 MPa when the content of TBP/OK was 18%. The loss of compressive strength of SPT was less than 10% after immersion and less than 25% after freeze-thaw treatment. The final setting time was 40.0 h, and the shrinkage of SPT was nearly 3%. The leaching test indicated that the release of TBP/OK from hardened SPT was limited. Characterization of SPT suggested that solidification of TBP/OK using PAG occurred by physical encapsulation.

1. Introduction

Radioactive tributyl phosphate (TBP) is a kind of waste organic solvent containing a variety of radionuclides (such as U and Pu) produced during the plutonium uranium recovery by extraction (PUREX) process for spent fuel reprocessing. The main components of this liquid are TBP, which can be used as an extractant, and kerosene (OK), which can be used as a thinner, and these components are affected by chemical and radioactive factors. Treating and disposing of the combustible organic solvent has become an urgent problem.

Large-volume Portland cements [1] were prepared to solidify TBP/OK organic liquids, and the emulsification-solidification and adsorption-emulsification-solidification methods were compared. The TBP/OK contents in the solidified materials prepared by the two methods were 15% and 18%, and the compressive strengths of the solidified forms were 11.4 MPa and 9.3 MPa, respectively. The results of the adsorption-solidification method [2] showed that the encapsulation capacity of slag cement mixed with an activated carbon adsorbent was better than that of Portland cement. The proportion of TBP/OK liquids encapsulated by

slag cement was 14%, and the mechanical properties and the soak resistance of the samples solidified by slag cement conformed to the requirements of GB14569.1-2011 [3]. Zhang et al. [4] studied the solidification of TBP/OK organic liquid by sulfur aluminate cement. Zeolite, calcium hydroxide, and MR-1 type emulsifier were mixed into the cement blends to improve the performance of the solidified waste. When the specification requirements were met, the compressive strength of the solidified samples reached 14.23 MPa, and the other material properties conformed to GB14569.1-2011. The TBP/OK organic solution was hydrolyzed and then solidified by alkali slag cementitious materials [5]. The compressive strength of the solidified forms was 18.9 MPa, and the TBP/OK content was 14.49%. The nuclide leaching rate and immersion resistance conformed to the Chinese specifications. This method requires the addition of NaOH to the TBP/OK organic solution, followed by heating. A high degree of corrosivity is required for the equipment, and it is thus not easy to apply this method on a large scale.

Recently, many countries have been developing new materials to solidify the radioactive waste. The Russian

State Atomic Energy Corporation (ROSATOM) [6] developed a new polymer material that can be used to solidify TBP and mixed (water-organic biphasic) sludge. A solidification experiment was conducted on a simulated radioactive organic liquid containing alkali-activated metakaolin base polymers [7], and the amount of organic liquid solidified reached 20%.

It can be noticed that the strength of TBP/OK solidified forms by cement was not more than 20 MPa. The productions of Portland cement, slag cement, and sulfur aluminate cement are characterized by high energy consumption and serious pollution, while geopolymers are environmentally friendly and green materials [8]. Sodium silicate-metakaolin geopolymers have been applied to solidify heavy metals, nuclear waste, and oil [9, 10]. PAG is synthesized in an acidic environment and has higher strength, durability, and thermal stability than sodium silicate-metakaolin geopolymers [11]. Research on the technology and mechanism of solidification of radioactive TBP/OK organic liquids by PAG is of interest.

In this paper, phosphoric acid and metakaolin are used to prepare PAG, and T80 is employed as an emulsifier. The paste fluidity, setting time, mechanical properties, leaching rate of TBP/OK, and pore structure of SPT are studied, and the mechanism of solidification of TBP/OK is discussed.

2. Materials and Experimental Methods

The kaolin used in this work mainly consisted of SiO_2 (45.35 wt.%), Al_2O_3 (39.22 wt.%), and Fe_2O_3 (0.31 wt.%). Kaolin was treated at the selected temperature of 800°C for 4 h in a muffle furnace. The obtained specimen (metakaolin) was cooled in air to ambient temperature and then stored in a dry environment.

The preparation of the solidified SPT samples is shown in Figure 1. The molar concentration of H_3PO_4 was 11 mol/L. The proportion of TBP/OK was defined as the weight of TBP/OK relative to the weight of all reactants. SPT containing 6% TBP/OK (CST), SPT containing 12% TBP/OK (DST), and SPT containing 18% TBP/OK (EST) were prepared. The dose of the emulsifier T80 was 4 vol% relative to the TBP/OK organic liquid content. The TBP/OK organic liquid was prepared by mixing OK and TBP at a volume ratio of 7:3. T80 was added to the TBP/OK organic liquid, and then phosphoric acid solution was added. The liquid mixture was treated with an ultrasonic disperser to prepare the emulsion (Figure 2). The emulsion and metakaolin were added to a stirring pot and stirred for 15 minutes to obtain fresh SPT (the mixing pot and mixing blade were made of 304 stainless steel). A Vicat apparatus was used to measure the initial and final setting times. The curing temperature was 70°C , and the humidity was more than 98%; while the room temperature was 36.4°C , and the humidity was 65%. Each setting time test was repeated 4 times, and the arithmetic mean was selected. Fresh SPT was poured into polypropylene (PP) plastic molds, and the samples were vibrated on a vibrating table for 3 minutes and then cured at 70°C and greater than 98% humidity for 7 days. The samples were removed from the molds after 7 days and were then

cured at 40°C in an oven for 28 days. Shrinkage of the $25\text{ mm} \times 25\text{ mm} \times 250\text{ mm}$ hardened PAG and SPT was measured with a shrinkage-compensating concrete expansion rate tester, and $\text{O}50\text{ mm} \times 50\text{ mm}$ samples were used to measure the strength (Figure 3).

After 28 days, the CST, DST, and EST samples were dipped in deionized water at $25 \pm 1^\circ\text{C}$ for 42 days (Figure 4), and the strength was tested again. Hardened PAG, CST, DST, and EST samples sealed in packets were put in a freezer at a temperature of -20°C for 3 h. The samples were removed from the freezer and immediately thawed in a water tank at 18°C . The thawing time was 4 h. The samples were subjected to five freeze-thaw cycles, and then their appearance was observed, and their compressive strength was tested. The amount of leached TBP/OK in the soaking solution was measured by gas chromatography.

Fragments of the PAG, CST, DST, and EST samples were collected and dipped in ethyl alcohol. The fragments were dried in an oven at 105°C for 12 h before testing. The porosity was tested by Mercury intrusion porosimetry (MIP) experiments. An MIP instrument (Autopore IV 9500, Micromeritics) was used to measure the pore size distributions. Other dried fragments of samples were milled into powders and used for XRD measurements, FTIR, and MAS NMR experiments. XRD was conducted by using a Bruker D8 ADVANCE instrument under the following conditions: 40 kV, 40 mA, and $\text{CuK}\alpha$ radiation. The range of the 2θ scanning angle was between 5° and 80° . FTIR experiments were performed by using a VECTOR33 FTIR spectrometer. The samples were mixed with KBr, and the wavelength was varied from 400 cm^{-1} to 4000 cm^{-1} .

3. Results and Discussion

3.1. Workability of Fresh SPT. Fresh PAG has a fluidity of 9.8 cm, as shown in Figure 5. The fluidity of fresh CST, DST, and EST is proportional to the TBP/OK content, and the fluidity increased from 13.0 cm to 15.5 cm (Figure 5). Metakaolin has a layered structure, and water and H_3PO_4 fulfill the voids, reducing the lubricity of the slurry. Furthermore, H_3PO_4 has a certain viscosity that decreases the fluidity of fresh PAG. T80 was added as a surfactant, which reducing the interfacial tension between the TBP/OK and the aqueous phase. When TBP/OK was added to the phosphoric acid solution, TBP/OK droplets were formed after ultrasonic dispersion.

Figure 6 shows the distribution of droplets in the CST, DST, and EST samples. When the solidified samples were broken, the droplets were removed, and spherical holes were left. More holes appeared in the solidified samples as the TBP/OK content increased. After emulsion, the organic droplets were surrounded by an outer hydrophilic layer to form spherical droplets. Spherical droplets distributed in phosphoric acid solution play a dominant role in lubrication. Therefore, the fluidity of the solidified forms increased with increasing encapsulation capacity. When metakaolin and the emulsion were mixed, the greater number of droplets reduced the surface tension of the liquid and resulted in better fluidity. This increase in droplets also caused more air to be

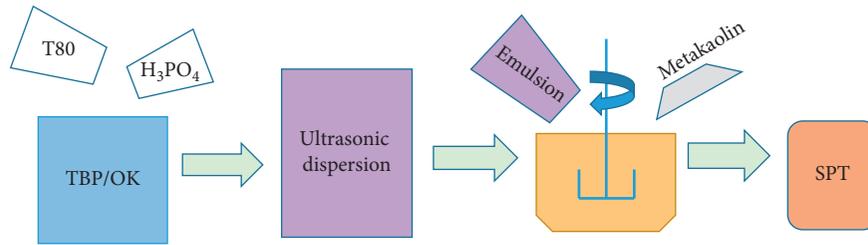


FIGURE 1: Preparation of the solidified SPT.



FIGURE 2: TBP/OK and H₃PO₄ emulsion.

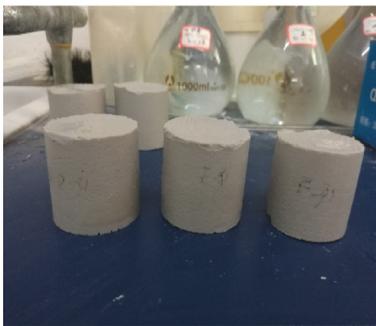


FIGURE 3: Hardened solidified SPT samples.

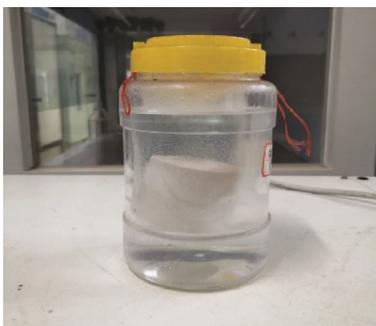


FIGURE 4: Leaching test of TBP/OK.

present in the solidified paste, and the porosity increased with the increase in the TBP/OK content.

When TBP/OK emulsions were mixed with metakaolin, the contact between the metakaolin powder particles and phosphoric acid decreased. Water molecules in the outer layer of droplets vaporized slowly, and dihydroxylation of the geopolymer slowed. These processes extended the setting

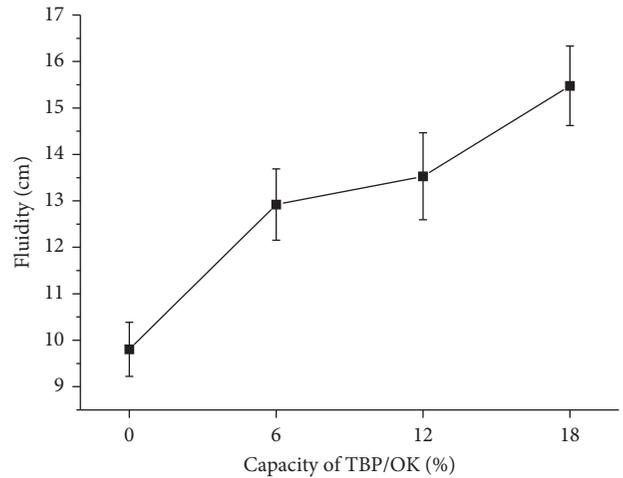


FIGURE 5: Fluidity of the solidified SPT samples with different TBP/OK contents.

time of the CST, DST, and EST samples. As shown in Figure 7, the initial setting time increased from 29.4 h to 30.6 h, and the final setting time increased from 35.7 h to 40.0 h. These long setting times limit the application of PAG in solidification.

3.2. Mechanical Properties of Hardened SPT. There was an obvious linear shrinkage of the PAG samples (3.2%), and the shrinkage of CST, DST, and EST was nearly 2.9% (Figure 8). As expected, the compressive strength decreased when the TBP/OK content increased. PAG has a high compressive strength of 79.07 MPa, and the strength of SPT is up to 59.19 MPa. The compressive strength did not decrease drastically with increasing TBP/OK content (Figure 9). When the composite contained 18% TBP/OK, the decrease in the compressive strength was 25%. These results indicate that the PAG is a rigid material with good mechanical properties. After the immersion test and freeze-thaw test, there were no obvious cracks on the surfaces of the PAG, CST, DST, and EST samples. The loss of compressive strength after immersion was less than 10%, and the loss of compressive strength after freeze-thaw treatment was less than 25% (Figure 10). These results indicated that the mechanical properties of SPT meet the requirements of the Chinese regulations “Performance Requirements for Low and Medium-Level Radioactive Waste Solidified Forms—Cement Solidified Forms.”

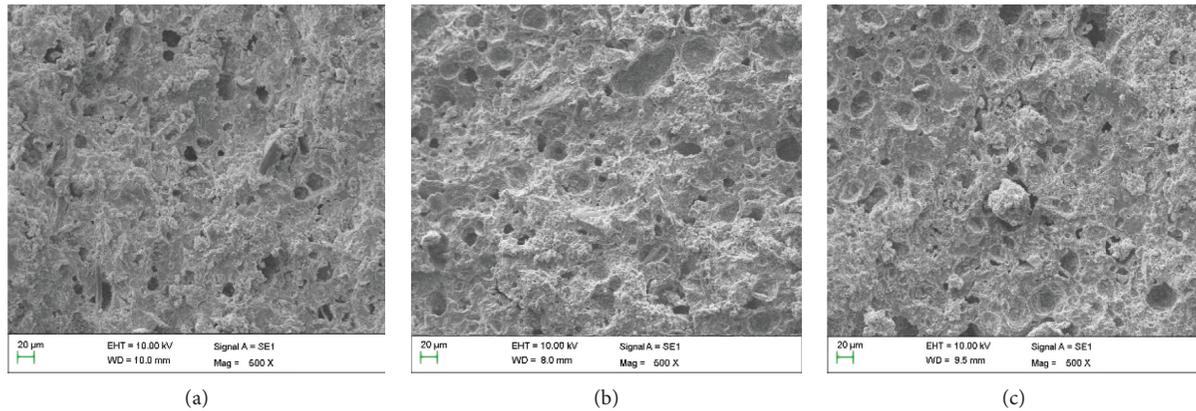


FIGURE 6: Distribution of droplets in the CST (a), SDT (b) and EST (c) samples.

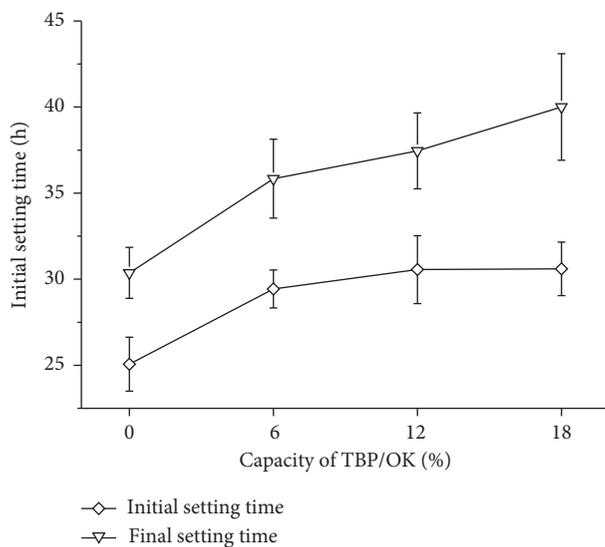


FIGURE 7: Setting time of the solidified SPT samples with different TBP/OK contents.

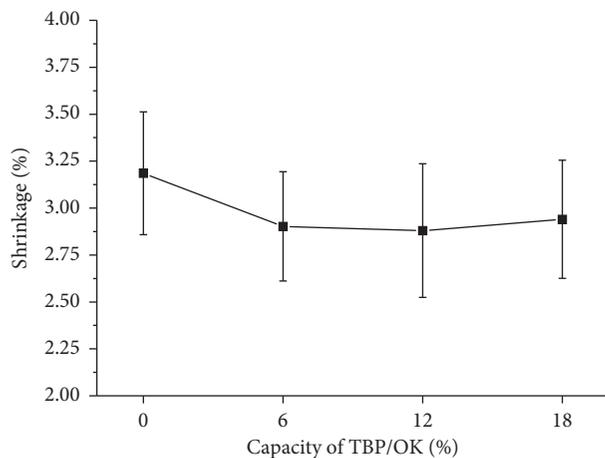


FIGURE 8: Shrinkage of the solidified SPT samples with different TBP/OK contents.

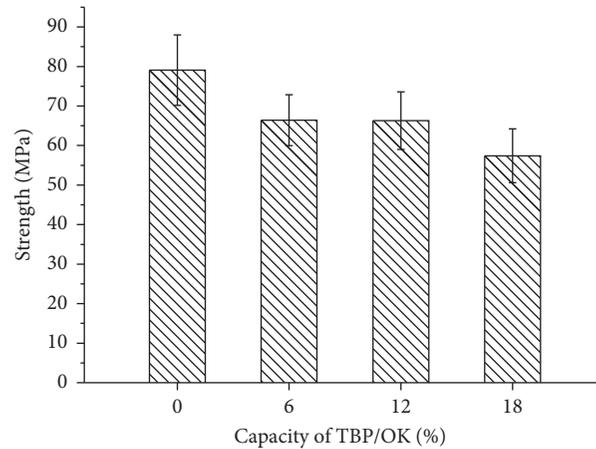


FIGURE 9: Compressive strength of the solidified SPT samples with different TBP/OK contents.

3.3. Compositions of Hardened SPT. A comparison between the X-ray diffraction patterns of the studied kaolin (KA) and calcined kaolin (MK) shows that all diffraction peaks corresponding to kaolin disappeared after heat treatment. Diffraction peaks corresponding to quartz were observed in the calcined kaolin diffraction patterns, while peaks corresponding to quartz and AlPO_4 crystal were observed in the PAG and SPT diffraction patterns (Figures 11 and 12). AlPO_4 was formed from the Al^{3+} in metakaolin and PO_4^{3-} from the H_3PO_4 solution. This indicates that the quartz remained unaffected during the geopolymerization process. The X-ray diffraction patterns of PAG and SPT exhibit an amorphous characteristic in the 2θ range of $15\text{--}20^\circ$. This indicates that the structures of PAG and SPT are typically glass-like.

In agreement with the X-ray diffraction results, FTIR spectra show the disappearance of metakaolin bands and the appearance of new bands that are related to new species (Figures 13 and 14). For calcined kaolin, the bands at 907 cm^{-1} ascribed to Al(VI)-OH disappeared as $-\text{OH}$ desorbed during the heating process. Bands at 805 cm^{-1} , 688 cm^{-1} , and 568 cm^{-1} ascribed to $-\text{Si-O-Al(IV)}$, $-\text{Si-O-}$

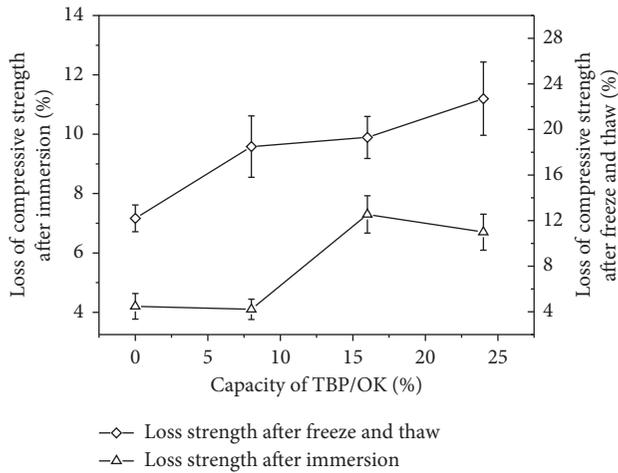


FIGURE 10: Loss of compressive strength of the solidified SPT samples with different TBP/OK contents.

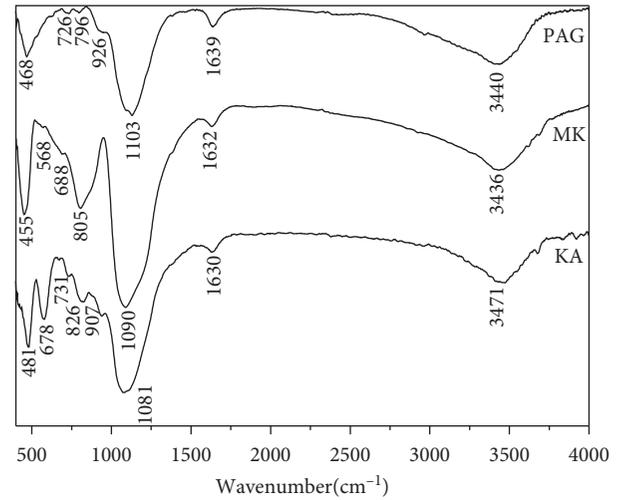


FIGURE 13: FTIR spectra of kaolin (KA) [12], calcined kaolin (MK) [12], and phosphate acid-based geopolymer (PAG).

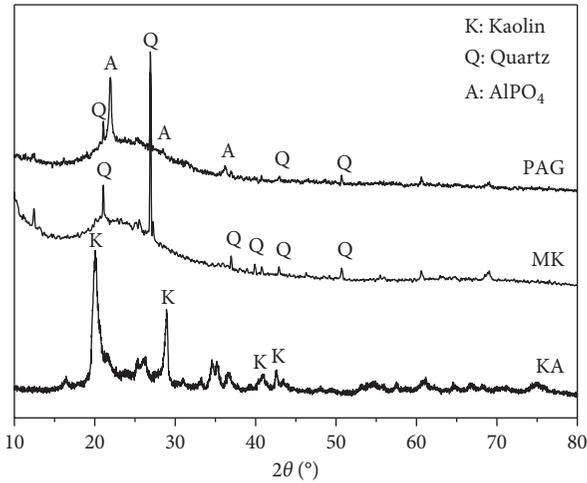


FIGURE 11: X-ray diffraction patterns of kaolin (KA) [12], calcined kaolin (MK) [12], and phosphate acid-based geopolymer (PAG).

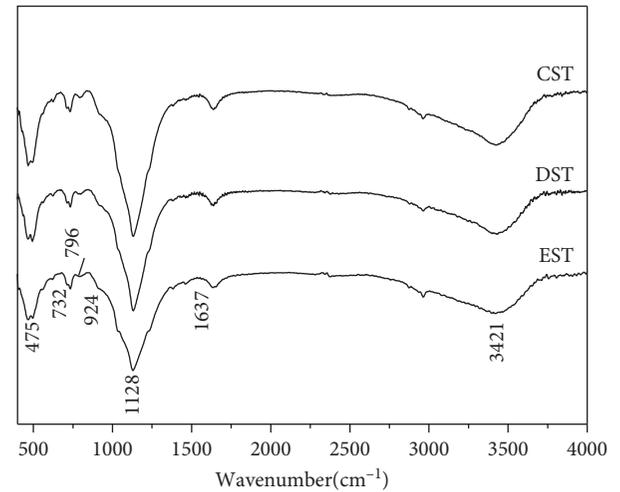


FIGURE 14: FTIR spectra of the PAG-solidified CST, DST, and EST samples.

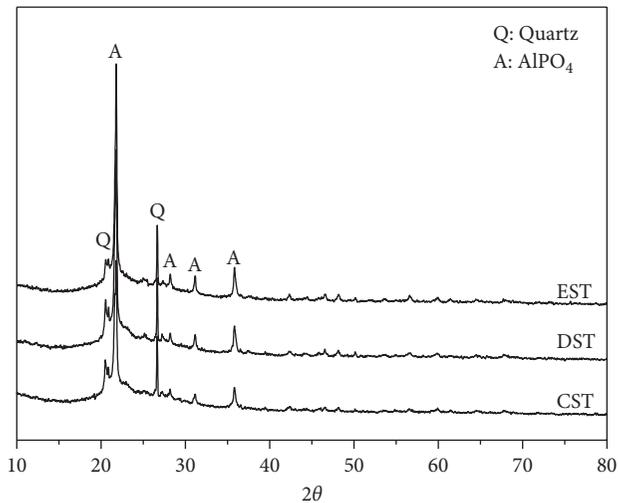


FIGURE 12: X-ray diffraction patterns of the PAG-solidified CST, DST, and EST samples.

Al(V), and -Si-O-Al(VI), respectively, appeared in the spectra of calcined kaolin. These bands disappeared after geopolymerization, and new bands at 726 cm^{-1} , indicative of the formation of -P-O-Al-, were observed in the spectra of PAG [12]. The bands at 926 cm^{-1} are attributed to -P-O-P- vibrations [12, 13].

The Si-O symmetrical vibration of metakaolin at 1090 cm^{-1} shifted by approximately 13 cm^{-1} to 1103 cm^{-1} after geopolymerization. In the spectra of PAG, new bands at 796 cm^{-1} could be attributed to -Si-O-P- [14]. The bands at 455 cm^{-1} in the metakaolin spectrum, which could be ascribed to -Si-O-Si-, shifted to a higher wavenumber of 468 cm^{-1} in the hardened PAG spectrum. This shift indicates that Si-O was converted to -Si-O-P- [9]. This may be attributed to the partial replacement of the [SiO] tetrahedra by [PO] tetrahedra, thus resulting in a change in the local chemical environment. This implies that the formation of -Si-O-P-O-Si- occurred in the geopolymer network [15].

TABLE 1: Leaching rates of TBP/OK in PAG-solidified TBP/OK samples (SPT).

Samples	α (%)	Leaching of TBP/OK at 25°C 10 ⁻³ /(cm·d ⁻¹)									P ₄₂ 10 ⁻² (cm)
		1 d	3 d	7 d	10 d	14 d	21 d	28 d	35 d	42 d	
CST	6	11.37	1.85	0.79	0.98	0.89	0.36	0.36	0.34	0.30	3.42
DST	12	12.16	2.11	1.04	1.29	0.97	0.49	0.44	0.42	0.41	4.13
EST	18	13.74	2.41	1.00	1.34	1.01	0.46	0.45	0.44	0.44	4.32

α : capacity of TBP/OK; P₄₂: cumulative leaching rate for 42 days (cm).

TABLE 2: Porosity and pore size distribution of PAG-solidified TBP/OK samples (SPT).

Samples	Pore size distribution				Porosity (%)
	≤10 nm	10–100 nm	100–1000 nm	≥1000 nm	
PAG	40.72	46.11	4.18	8.99	16.94
CST	35.52	47.66	7.58	9.24	17.44
DST	30.24	50.15	7.77	11.84	22.03
EST	26.82	52.36	8.59	12.23	23.47

In Figure 14, in the spectra of the CST, DST, and EST samples, the bands at 924 cm⁻¹ were attributed to -P-O-P- vibrations [12, 13]. New bands at 732 cm⁻¹ are in agreement with the formation of -P-O-Al-. The metakaolin bands at 455 cm⁻¹ ascribed to -Si-O-Si- shift to a higher wavenumber of 475 cm⁻¹ in the spectra of the hardened samples. Furthermore, new bands at 796 cm⁻¹ related to -Si-O-P- were observed. The Si-O symmetrical vibration of metakaolin at 1090 cm⁻¹ shifted to 1128 cm⁻¹ after solidification. This indicates that the network structure of SPT comprises -Si-O-P-O-Si- and -P-O-Al- as well [12]. The products were nearly the same for PAG and SPT. Solidification of TBP/OK could occur by physical encapsulation.

3.4. Leaching Test of TBP/OK. The cumulative amounts of TBP/OK released into the leachates from SPT composite samples containing 6–18% TBP/OK at 25 ± 1°C are reported in Table 1. The cumulative quantity of TBP/OK released in the leachate increased slowly during the first two weeks of the experiment and then tended to remain stable for the remaining 42 days. The cumulative leaching rates of the CST, DST, and EST samples for 42 days were 3.42 × 10⁻² cm, 4.13 × 10⁻² cm, and 4.32 × 10⁻² cm, respectively.

The pore size distribution of PAG and SPT is shown in Table 2. Most pore size diameters were smaller than 100 nm in PAG, CST, DST, and EST. The number of pores smaller than 10 nm decreased, while the number of pores between 10 nm and 100 nm increased. The number of pores larger than 1000 nm also increased in the CST, DST, and EST samples. The presence of emulsified droplets increased the setting time and prevented water molecules from evaporating, causing an increase in the pore size of SPT. The porosity increased with increasing TBP/OK content. The results demonstrate that TBP/OK was efficiently encapsulated in SPT and met the nuclear authorities' acceptance criteria for waste storage applications.

3.5. Discussion of Experimental Errors. To ensure the reliability of the data, including the measured compressive

strength, fluidity, shrinkage, and loss of compressive strength of the solidified samples, 6 samples of each group were prepared for testing. The arithmetic mean of the values in one group of each experiment was selected as the result. If a test value in one group was larger or less than 15% of the arithmetic mean, all values in this group were discarded. The standard deviations of compressive strength were 8.91%, 6.44%, 7.28%, and 6.82%, and those of shrinkage were 0.35%, 0.29%, 0.36%, and 0.31%. The standard deviations of fluidity ranged from 0.58% to 0.94%. The standard deviations of loss of compressive strength after immersion and after freeze-thaw treatment ranged from 0.34% to 0.61% and from 1.17% to 3.02%, respectively. For setting time test, each test was repeated 4 times, and the arithmetic mean was selected. Six samples from each group were used to measure the leaching of TBP/OK and the porosity. The arithmetic mean of each experiment was selected as the result. The leaching of TBP/OK in Table 1 and porosities in Table 2 were the arithmetic means.

4. Conclusion

A method of solidifying spent TBP/OK organic liquids with phosphate acid-based geopolymer was investigated. The main findings of this study can be summarized as follows.

TBP/OK organic liquids can be solidified in PAG, and the stability of the TBP/OK emulsion in the phosphate acid solution and in the geopolymer paste during mixing allows the encapsulation of high TBP/OK contents in the composite (up to 18%).

The compressive strength of the SPT was up to 59.19 MPa when the content of TBP/OK was 18%. The loss of compressive strength of SPT was less than 10% after immersion and less than 25% after freeze-thaw treatment.

The fluidity of fresh SPT is 15.5 mm, the final setting time was 40.0 h, and the shrinkage of SPT was nearly 3% when the content of TBP/OK is 18%.

Leaching tests demonstrated that a very limited amount of TBP/OK was released from the PAG-solidified TBP/OK samples. Solidification of TBP/OK could occur by physical encapsulation.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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References

- [1] D. H. Du, L. Gong, and L. Cheng, "Study on the formulation of mass-pouring cement used to solidified organic waste liquid," *Radiation Protection*, vol. 12, no. 5, pp. 364–372, 1992.
- [2] Z. Y. Chen, W. L. Huang, G. Q. Zhang, Y. J. Zhang, and J. S. Zhang, "Study on the formulation of cement solidification of 30% TBP/OK organic liquid waste," *Atomic Energy Science and Technology*, vol. 25, no. 4, p. 74, 1991.
- [3] CSBTS, *Characteristic Requirements for Solidified Waste of Low and Intermediate Level Radioactive Waste-Cement Solidified Waste (GB14569.1-2011)*, CSBTS, Beijing, China, 2011.
- [4] W. Zhang, J. Li, and J. Wang, "Solidification of spent radioactive organic solvent by sulfoaluminate and Portland cements," *Journal of Nuclear Science and Technology*, vol. 52, no. 11, pp. 1362–1368, 2015.
- [5] R. Hua, Z. B. Zhang, S. J. Liu, and M. B. Lou, "Solidification of spent tributyl phosphate by alkali-activated slag," *Atomic Energy Science and Technology*, vol. 47, no. 11, pp. 1956–1960, 2013.
- [6] Y. Pokhitonov, V. Babain, and V. Kamachev, "Russian: result and prospects of liquid solidification experiments at ROSA-TOM sites," in *Proceedings of the ASME 2011 14th International Conference on Environmental Remediation and Radioactive Waste Management ICEM2011*, Reims, France, September 2011.
- [7] V. Cantarel, F. Nouaille, A. Rooses, D. Lambertin, A. Poulesquen, and F. Frizon, "Solidification/stabilisation of liquid oil waste in metakaolin-based geopolymer," *Journal of Nuclear Materials*, vol. 464, pp. 16–19, 2015.
- [8] S. Z. Zhang and K. C. Gong, "Geopolymer," *Materials Science and Engineering*, vol. 21, no. 3, pp. 430–436, 2003.
- [9] K. L. Li, "Solidification analysis of heavy metal and radioactive metal by alkali-activated cement," *Journal of Building Materials*, vol. 16, no. 2, pp. 310–314, 2013.
- [10] J. Davidovits, *Geopolymer Chemistry and Applications*, National Defense Industry Press, Beijing, China, 2011.
- [11] D. S. Perera, J. V. Hanna, J. Davis et al., "Relative strengths of phosphoric acid-reacted and alkali-reacted metakaolin materials," *Journal of Materials Science*, vol. 43, no. 19, pp. 6562–6566, 2008.
- [12] T. Dong, S. B. Xie, J. S. Wang, Z. F. Chen, and Q. Liu, "Properties and characterization of a metakaolin phosphate acid-based geopolymer synthesized in a humid environment," *Journal of the Australian Ceramic Society*, 2019.
- [13] N. R. Yang and R. H. Yue, *The Handbook of Inorganic Matalloid Materials Atlas*, Wuhan University of Technology Press, Wuhan, China, 2000.
- [14] L. Stoch and M. Šoc, "Infrared spectroscopy in the investigation of oxide glasses structure," *Journal of Molecular Structure*, vol. 511-512, pp. 77–84, 1999.
- [15] H. K. Tchakouté and C. H. Rüschler, "Mechanical and microstructural properties of metakaolin-based geopolymer cements from sodium waterglass and phosphoric acid solution as hardeners: a comparative study," *Applied Clay Science*, vol. 140, pp. 81–87, 2017.

