



Article The Design and Verification of a TBP/OK Pyrolysis Incineration Stable System

Jing Ma, Jingyu Zhao *[©], Tiejun Liu, Cuiling Yang, Yeyun Wang, Jinghui Zhang, Mingfu Li and Yufan Sun

China Nuclear Power Engineering Co., Ltd., China National Nuclear Corporation, Beijing 100048, China

* Correspondence: zhaojingyu2017@126.com

Abstract: This project designed and created a large-scale pyrolysis incineration system that decomposes waste tributyl phosphate/kerosene (TBP/OK) solvent from the plutonium/uranium process (PU-REX) in the nuclear industry. This system consists of a suspension preparation system (SPS), a pyrolysis and ash discharge system (PADS), and a combustion furnace and gas treatment system (CGS). The preparation of a waste TBP/OK emulsified suspension in the SPS, continuous operation experiments of the PADS and CGS, and pyrolysis incineration experiments were conducted. The results show that the SPS achieved the automatic preparation and feeding of emulsified suspensions at 30 kg/h. The PADS decomposed 99.99% of the TBP/OK emulsified suspensions and fixed more than 99% of phosphorus. The CGS burned the pyrolysis gas without diesel oil and purified more than 99.995% of the radioactive nuclides. This system showed great feasibility, stability, continuity, and safety, proving the compatibility between multiple systems of this new design. This paper marks a significant step in pyrolysis incineration technology for the nuclear industry.

Keywords: pyrolysis incineration; TBP/OK; PUREX

check for updates

Citation: Ma, J.; Zhao, J.; Liu, T.; Yang, C.; Wang, Y.; Zhang, J.; Li, M.; Sun, Y. The Design and Verification of a TBP/OK Pyrolysis Incineration Stable System. *Processes* **2023**, *11*, 1338. https://doi.org/10.3390/ pr11051338

Academic Editor: Fausto Gallucci

Received: 28 March 2023 Revised: 21 April 2023 Accepted: 25 April 2023 Published: 26 April 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/).

1. Introduction

Tributyl phosphate (TBP) is a widely used extractant in the nuclear industry and kerosene (OK) is selected as the diluent of TBP for the separation of uranium and plutonium in most cases [1]. After several extraction cycles, the performance of the TBP/OK solvent reduces because of the irradiation of radionuclides, such as 90Sr and 137Cs [2,3]. Thus, the treatment of radioactive waste organic solvent TBP/OK [4,5] is essential in the plutonium uranium reduction extraction process (PUREX) [6-8]. Many advanced methods have been applied to treat this organic waste solvent, such as pyrolysis [9,10], steam reforming [11], supercritical water oxidation [12,13], wet oxidation [14,15], and electrochemical catalytic oxidation [16,17]. However, there are too many problems with some technologies, making it very difficult to apply them in the nuclear industry at present. For example, H_3PO_4 generated by decomposed TBP may cause serious corrosion to the equipment in steam re-forming and the supercritical water oxidation technique. Direct incineration of TBP will produce large amounts of radionuclide-containing waste gas, which is a great threat to the ecological environment. Wet oxidation and electrochemical catalytic oxidation will generate a large quantity of radioactive waste liquid. Thus, considering the complexity, corrosivity, and radioactivity of waste TBP/OK solvent, pyrolysis incineration is the only mature and reliable technology that can be used in large-scale engineering applications.

Pyrolysis is a flameless, retorting process, where organic matter is isolated from the air or oxygen and externally heated and pyrolyzed into volatile components with a high calorific value. The main products are usually methane, ethane, benzene, toluene, tar, and coke, and the general pyrolysis temperature of organic matter is 500~600 °C. Currently, pyrolysis technology is widely used in organic waste treatment. Jouhara's study showed that organic materials (organic tissue, plastic bottles, and nappies) could be pyrolyzed into bio-oil, which has a calorific value close to gasoline [18]. Ding's study

indicated that the pyrolysis products of biomass, plastic, and paper could be controlled by the pyrolysis temperature [19]. Miranda's studies proved that plastic pyrolysis in a vacuum could enhance the efficiency and generate more environmentally friendly pyrolysis products [20–22]. However, few studies have been conducted on the pyrolysis of waste TBP produced in the nuclear industry.

In 1999, the Belgoprocess was conceived, using a spherical bed pyrolysis reactor to treat waste TBP/OK solvent generated from the PUREX process with $Ca(OH)_2$ [23]. This technology pumps liquid waste into a pyrolytic furnace with many removable steel balls. These moving steel balls can improve the thermal transduction effect and grind up the solid pyrophosphate and excess limestone produced by pyrolysis. At 350–600 °C, the waste TBP/OK solvent decomposes into phosphoric acid and hydrocarbons, and the resulting phosphoric acid reacts with $Ca(OH)_2$ in the suspension to form calcium pyro-phosphate. The related reactions are as follows [1]:

$$(C_4H_9O)_3PO \rightarrow 3C_4H_8 + H_3PO_4$$

 $2H_3PO_4 + 3Ca(OH)_2 \rightarrow Ca_3(PO_4)_2 + 6H_2O$

 $2(C_4H_9O)_3PO + 2Ca(OH)_2 \rightarrow Ca_2P_2O_7 + 6C_4H_8 + 5H_2O$

$$2(C_4H_9O)_3PO + 2Ca(OH)_2 + H_2O \rightarrow Ca_2P_2O_7 + 6C_4H_9OH$$

Finally, the resulting pyrolysis ash is collected at the bottom of the furnace. The fan transfers hydrocarbon gas to the combustion chamber. It is then burned at about 1000 $^{\circ}$ C to convert into CO₂ and water.

The waste TBP/OK solvent treatment system had many core facilities, including a pyrolytic furnace, feed pump, high-temperature gas filter, combustion furnace, and scrubbing towers. From previous studies [24], many problems need to be solved, such as a blocked high-temperature gas filter, a pyrolysis furnace with a stuck paddle, an incinerator operating at an unexpectedly high temperature, and an overloaded exhaust fan. Besides that, equipment corrosion by phosphoric acid, which comes from the pyrolysis of TBP, is another critical problem that needs to be settled.

So, in this project, an experimental system was designed to optimize and improve the difficulties of the large-scale application of pyrolysis incineration of waste TBP/OK solvent. Many necessary experiments were performed to study the optimum processing conditions. The compatibility between multiple systems and the feasibility, stability, continuity, safety of the systems were verified.

2. Design and Experiments

2.1. System Design

This project designed and built an experimental system to simulate the treatment of waste TBP/OK solvent, and the system consists of suspension preparation system (SPS), pyrolysis and ash discharge system (PADS), and combustion furnace and gas treatment system (CGS) as shown as Figure 1. SPS was used for preparation and feeding emulsified suspensions. This system is mainly composed of four tanks, which are respectively TBP/OK receiving tanks, emulsifier preparation tank, suspension preparation tank and emulsified suspension tank (feeding tank), respectively. The Ca(OH)₂ (or Mg(OH)₂) and water were added in emulsifier preparation tank in a certain proportion to form emulsifier, which was pumped to suspension preparation tank and mixed with TBP/OK to form emulsified suspension. Then this emulsified suspension was pumped to feeding tank for further processing. PADS was mainly consists of pyrolysis furnace, ash tank, high-temperature gas filter and ash discharge components. The TBP/OK emulsified suspension was decomposed to pyrolysis ash and pyrolysis gas in pyrolysis furnace under high temperature. The pyrolysis ash was collected in ash tank and then transported to ash drums by ash discharge

components for further disposal. The pyrolysis gas was purified by high-temperature gas filter and then flowed to combustion furnace. CGS was similar to a conventional incineration system, which was consisted of combustion furnace and off-gas purification system. The pyrolysis gas was burned into CO_2 and H_2O in incineration furnace, and the generated off-gas was discharged to air after several scrubbing and filtration.



Figure 1. (a) Full process flow diagram, (b) suspension preparation system (SPS), (c) pyrolysis and ash discharge system (PADS), and (d) combustion furnace and gas treatment system (CGS) in the pyrolysis incineration of waste TBP/OK solvent.

Full process of pyrolysis incineration TBP/OK was described in Figure 1a, the waste TBP/OK solvent was added to TBP/OK receiving tank and passed SPS, PADS, and CGS in sequence. After treatments, the pyrolysis ash was collected in ash drums, and the pyrolysis gas was burned in a combustion furnace. Finally, the combustion products were discharged into the air after condensation and purification.

2.2. Materials and Characterization

Tributyl phosphate (TBP), cesium chloride (CsCl), and strontium chloride (SrCl₂) were obtained from Aladdin Reagent Company. Calcium hydroxide (Ca(OH)₂), magnesium hydrate (Mg(OH)₂), kerosene (OK), diesel oil, and commercial surfactants were purchased

from Real & Lead Chemical Reagent Co., Ltd. (Tianjin, China). All reagents were pure analytical grade except for TBP, kerosene (OK), and diesel oil.

High-performance liquid chromatography (HPLC) was used to test the organic components of the liquid. P, Sr, and Cs concentrations in the pyrolysis gas condensate and the washing liquid in the scrubber were measured by inductively coupled plasma optical emission spectrometry (ICP-OES) or inductively coupled plasma mass spectrometry (ICP-MS). Liquid samples were diluted to a suitable concentration and tested directly, while solid samples were dissolved first. The emulsified suspensions' viscosities were tested by a viscometer at room temperature.

2.3. Experiments

The following experiments were conducted in the waste TBP/OK solvent treatment system:

- I. Preparation of a waste TBP/OK emulsified suspension with Ca(OH)₂ or Mg(OH)₂ in the suspension preparation system (SPS):
 - (a) A study of the properties of different TBP/OK emulsified suspensions. In this project, four different emulsified suspensions were prepared and the viscosity (mPa.s), density (kg/m³), stability (day), and emulsification time (min) of these samples were tested.
 - (b) A stability test for continuous feeding of TBP/OK emulsified suspensions. The wall-hanging or pipe-blocking problems were verified at the maximum treatment capacity of the SPS.
- II. The ongoing experiments of the pyrolysis and ash discharge system (PADS) and the combustion furnace and gas treatment system (CGS):
 - (a) A study of the influence of the number of grinding balls and the stirring paddle speed on the torque of the stirring paddle. The torque of the stirring paddle was tested at different filling rates of the grinding balls (0%, 25%, 50%, 75%, and 100%) and different speeds of the stirring paddle (1.5 rpm, 2.5 rpm, 4.0 rpm, 6.0 rpm, and 8.0 rpm).
 - (b) A study of the influence of different temperatures on the torque of the stirring paddle. The torque of the stirring paddle was tested at the different temperatures (from 23 $^{\circ}$ C to 400 $^{\circ}$ C) of the pyrolysis furnace.
 - (c) A study of the influence of pyrolysis ash on the torque of the stirring paddle. The torque of the stirring paddle was tested when pyrolysis ash (Ca(OH)2 particles were used to simulate the generated pyrolysis ash) was added to the pyrolysis furnace at different speeds of the stirring paddle (1.5 rpm, 2.5 rpm, 4.0 rpm, 6.0 rpm, and 8.0 rpm). Besides that, the efficiency of the ash discharge was verified by the painted grinding balls.
 - (d) A study of the incineration of pyrolysis gas in a combustion furnace. The different stages of pyrolysis gas combustion in the combustion furnace were observed to study the influence of diesel oil on the burning of pyrolysis gas. Additionally, the pressures in the pyrolysis furnace and combustion furnace were continuously tested to study the direction of the pyrolysis gas flow.
- III. Pyrolysis incineration of waste TBP/OK solvent with different emulsified suspensions (Ca(OH)₂ or Mg(OH)₂), specified in Table 1.

Emulsified Suspensions (Weight Percent)	Capacity (kg/h)	Duration (h)	Pyrolysis Temperature (°C)	Combustion Temperature (°C)
30% TBP with Ca(OH) ₂	6–8	48	400	850
60% TBP with Ca(OH) ₂	6–8	48	400	850
30% TBP with Mg(OH) ₂	6–8	48	400	850
60% TBP with Mg(OH) ₂	6–8	48	400	850

Table 1. The specific experimental conditions of the pyrolysis incineration of the waste TBP/OK solvent.

The following parameters need to be studied:

(a) Pyrolysis ratio: the pyrolysis ratio was calculated by Formula (1), where mTBP denotes the mass of TBP.

Pyrolysis ratio =
$$1 - \frac{m_{TBP} \text{ in pyrolysis gas}}{m_{TBP} \text{ in emulsified suspensions}}$$
 (1)

(b) Phosphorus fixation ratio: the phosphorus fixation ratio was calculated by Formula (2), where mp is the mass of P.

Phosphorus fixation ratio =
$$1 - \frac{m_P \text{ in pyrolysis gas}}{m_P \text{ in emulsified suspensions}}$$
 (2)

(c) Radioactive ion fixation ratio: the radioactive ion fixation ratio was calculated by Formula (3), where Cinitial is the initial concentration of the radioactive ions in the emulsified sus-pensions and $C_{2-scrubber}$ is the final concentration of the radioactive ions in scrubber 2.

Radioactive ions fixation ratio =
$$1 - \frac{C_{2-\text{scrubber}}}{C_{\text{initial}}}$$
 (3)

A sampling system consisting of a condenser, a liquid collector, and other ancillary equipment was designed to collect the pyrolysis gas for the above studies. When the sam-pling system was opened, the pyrolysis gas enters the condenser and condenses into a liquid to be collected. In order to ensure the safety of the system and the accuracy of the data, all the experiments were repeated more than three times.

3. Results and Discussion

3.1. Preparation of Waste TBP/OK Emulsified Suspension

In this project, to prevent the phosphoric acid generated from the decomposition of TBP from corroding the equipment, alkaline $Ca(OH)_2$ or $Mg(OH)_2$ emulsions were mixed with TBP/OK solvent to form emulsified suspensions before the pyrolysis process [4,25]. The prepared emulsified suspensions are shown in Figure 2, and the experimental parameters are shown in Table 2.

From Figure 2, all TBP/OK emulsified suspensions were uniformly milky white, which indicated that these four samples might have similar physical properties. The sta-bility of these emulsified suspensions was excellent because they lasted at least five days without stratification (especially 60% TBP with Mg(OH)₂, which remained in a homoge-neous emulsified state for 60 days), as shown in Table 2. Regardless of whether Ca(OH)₂ or Mg(OH)₂ suspensions were used, when the ratio of TBP increased from 30% to 60%, the viscosity and density of the suspensions showed an apparent increase. All the emulsified suspensions' viscosities varied from 50 to 100 mPa-s, an appropriate range for continuous feeding. The emulsification time of all suspensions was less than 40 min with stirring (100 rpm). These times are quick enough to operate the suspension preparation system (SPS) continuously.



Figure 2. Emulsified suspensions of (**a**) 30% TBP with $Ca(OH)_2$, (**b**) 60% TBP with $Ca(OH)_2$, (**c**) 30% TBP with Mg(OH)₂, and (**d**) 60% TBP with Mg(OH)₂.

Emulsified Suspensions	Viscosity (mPa.s)	Density (kg/m ³)	Stability (Day)	Emulsification Time (min)
30% TBP with Ca(OH) ₂	63.63	900	5	25
60% TBP with Ca(OH) ₂	84.52	994	5	25
30% TBP with Mg(OH) ₂	50.60	890	12	25
60% TBP with Mg(OH) ₂	55.45	980	60	40

Many experiments verified that the Suspension Preparation System (SPS) ran well with all emulsified suspensions. Figure 3 showed no wall-hanging or pipe-blocking problems when the system reached a maximum feeding capacity of 30 kg/h (12 kg/h TBP). This result was good enough for the following experiments and applications.



Figure 3. Continuous operation of the suspension preparation system (SPS).

3.2. Continuous Operation Pyrolysis and Ash Discharge System (PADS) and Combustion Furnace and Gas Treatment System (CGS) Experiments

The pyrolysis and ash discharge system (PADS) is the core of this project. The num-ber of grinding balls, pyrolysis temperature, and pyrolysis ash affect the performance. The combustion furnace and gas treatment system (CGS) deals with the products generated from the PADS.

3.2.1. Study of the Influence of the Number of Grinding Balls and Speed of the Stirring Paddle on the Torque of the Stirring Paddle

In most instances, the torque of the stirring paddle in the pyrolysis furnace is indicative of the pyrolysis performance. This comparison can be made because a greater torque means better grinding, which leads to a higher heat transfer efficiency. The influence of the number of grinding balls and the stirring paddle speed was studied on the torque of the stirring paddle. The torque of the stirring paddle could be measured and recorded by a sensor at the top of the stirring paddle. The changes in torque of the stirring paddle with the filling rate of the grinding balls and speed of the stirring paddle are shown in Figure 4a,b, respectively.



Figure 4. The changes in torque of the stirring paddle with (**a**) the filling rate of the grinding balls and (**b**) the speed of the stirring paddle.

Figure 4a,b indicate that the torque of the paddle increased with an in-crease in the filling rate of the grinding balls in the pyrolysis furnace. In addition, the speed of the stirring paddle did not have much impact on the torque of the paddle. This effect on the paddle is most significant in the case of a high filling rate of grinding balls.

3.2.2. Study of the Influence of Different Temperatures on the Torque of Stirring Paddle

The temperature in the pyrolysis furnace directly influences the pyrolysis of the TBP/OK solvent. Thus, it is vital to study the temperature variation during operation. Considering the safety of and temperature distributions in the pyrolysis furnace, the gradient heating method was chosen. The results are shown in Figure 5. The results indicate that the torque of the stirring paddle in the pyrolysis furnace increased with an increase in the temperature of the heating process. When the furnace temperature reached 400 °C, a suitable temperature for pyrolysis of TBP [24], the feeding operation began. The temperature in the furnace dropped a little and recovered in a few minutes. During that process, the torque was maintained at 2000 Nm, which is suitable for the pyrolysis of TBP/OK [24]. Thus, the stirring paddle torque was affected less by temperature.



Figure 5. The temperature and torque of the stirring paddle of the pyrolysis furnace in the heating and operation process.

3.2.3. Study of the Influence of Pyrolysis Ash on the Torque of Stirring Paddle

During pyrolysis, solid pyrolysis products are generated. These solid pyrolysis products mainly consist of small granular inorganic salts, such as calcium phosphate, calcium pyrophosphate, and calcium hydroxide. Their generation and accumulation may affect the pyrolysis of the TBP/OK solvent. In this paper, Ca(OH)₂ particles were added to the pyrolysis furnace to simulate the generation of pyrolysis ash. As a result, an ash dis-charge system was built.

As shown in Figure 6, the torque of the stirring paddle decreased a little within a few minutes after the addition of simulated pyrolysis ash (Ca(OH)₂ particles) and quickly re-covered to the average level. This indicates that the generation of the pyrolysis ash does not affect the performance of pyrolysis reactions. Indeed, the accumulation of pyrolysis ash would take up too much space in a pyrolysis furnace and the pyrolysis ash might stick to the surface of the grinding balls, resulting in a lower heat transfer efficiency. Thus, an efficient pyrolysis ash discharge system was necessary. As Figure 7 shows, a red pig-ment was painted on the grinding balls to test the efficiency of the ash discharge system. After about 4 min (cold operation without heating), the red pigment began to drain from the ash hopper, which proved the efficiency of the ash discharge system was sufficient to ensure the continuous operation of the pyrolysis and ash discharge system (PADS).



Figure 6. Torque of stirring paddle of pyrolysis furnace with adding of pyrolysis ash.



Figure 7. (a) Red-pigment-painted grinding balls and (b) ash hopper (after 4 min operation).

3.2.4. Study of the Incineration of Pyrolysis Gas in a Combustion Furnace

After the pyrolysis process, the TBP/OK emulsified suspension decomposes into pyrolysis ash (discharged by the PADS) and pyrolysis gas, composed of short-chain organic molecules (mainly C_4H_8). This pyrolysis gas flows into the combustion furnace to burn and become CO_2 , H_2O , and a few other products, and these products were cooled and fil-tered before being discharges into the air.

To study the heat storage capacity of the combustion furnace, when the temperature reached 850 °C, the igniter was turned off and atomized diesel oil was added to simulate the pyrolysis gas, as shown in Figure 8. The results showed that the combustion furnace could ignite atomized diesel oil at a high temperature. The pyrolysis gas was burned con-tinuously without diesel oil, as shown in Figure 9.

The pressures in the pyrolysis furnace and combustion furnace are shown in Figure 10. The results indicated that the generated pyrolysis gas could continuously flow to the combustion furnace. Additionally, the pressure difference between the pyrolysis furnace and the combustion furnace was maintained at 0–1 kPa, which ensures that the pyrolysis gas cannot return to the pyrolysis furnace from the combustion furnace during the incin-eration process.



Figure 8. Adding atomized diesel oil after turning off the igniter.



Figure 9. Pyrolysis gas burned continuously without diesel oil.





3.3. Pyrolysis Incineration of Waste TBP/OK Solvent with Different Emulsified Suspensions

The above experiments proved the feasibility, stability, and continuity of the suspension preparation system (SPS), pyrolysis and ash discharge system (PADS), and combustion furnace and gas treatment system (CGS). However, the performance of the pyrolysis incineration of waste TBP/OK solvent needs to be determined by the pyrolysis ratio, phosphorus fixation ratio, and radioactive ion fixation. In every experiment, 200 g of emulsified suspension, pyrolysis gas condensate, and scrubbing solution sample were taken to measure or calculate these parameters further.

3.3.1. Pyrolysis Ratio

The pyrolysis ratio directly reflects the decomposition of the TBP/OK solvent. A high pyrolysis ratio indicates a sufficient pyrolysis reaction. The system temperature, pressure, stirring speed, and other conditions meet the requirements for pyrolysis incineration of waste TBP/OK solvent. The results of the pyrolysis incineration of waste TBP/OK solvent with different emulsified suspensions are shown in Table 3.

Capacity (kg/h)	30% TBP with Ca(OH) ₂	60% TBP with Ca(OH) ₂	30% TBP with Mg(OH) ₂	60% TBP with Mg(OH) ₂
6	99.9908%	99.9915%	99.9826%	99.9918%
7	99.9930%	99.9940%	99.9773%	99.9916%
8	99.9928%	99.9947%	99.9831%	99.9919%

Table 3. Pyrolysis ratios of waste TBP/OK solvent with different emulsified suspensions.

As seen in Table 3, the pyrolysis ratios of TBP/OK solvent with different emulsified suspensions at the capacity of 6–8 kg/h were higher than 99.99% (except for 30% TBP with Mg(OH)₂, which is, however, very close to 99.99%). This indicates that the system showed an outstanding pyrolysis performance of TBP/OK solvent, which could meet the nuclear industrial needs.

3.3.2. Phosphorus Fixation Ratio

The phosphorus fixation ratio is another important parameter of pyrolysis incineration of waste TBP/OK solvent because the decomposition of TBP will generate a lot of phosphoric acids, which are highly corrosive. Generally, the system's lifetime is deter-mined by the phosphorus fixation ratio. The phosphorus fixation ratios of different emul-sified suspensions are shown in Table 4.

Table 4. Phosphorus fixation ratios of waste TBP/OK solvent with different emulsified suspensions.

Capacity (kg/h)	30% TBP with Ca(OH) ₂	60% TBP with Ca(OH) ₂	30% TBP with Mg(OH) ₂	60% TBP with Mg(OH) ₂
6	99.8475%	98.7618%	96.0498%	99.3392%
7	99.7304%	99.5263%	98.1259%	99.5526%
8	99.9195%	99.3850%	98.5061%	99.5829%

As seen in Table 4, the phosphorus fixation ratios of waste TBP/OK solvent with dif-ferent emulsified suspensions are similar to the pyrolysis ratios. Both Ca(OH)₂ and Mg(OH)₂ emulsions showed excellent phosphorus fixing ability. Only the 30% TBP with Mg(OH)₂ phosphorus fixation ratios were lower than 99%. The insufficient pyrolysis of TBP in 30% TBP with Mg(OH)₂ emulsified suspension may lead to this lower phosphorus fixation ratio. A high phosphorus fixation ratio (99%) ensured the system had a long enough lifetime to meet the requirements of the nuclear industry. From the results of py-rolysis ratio and phosphorus fixation ratio of these four different emulsified suspensions, it is clear that all of them have great potential for nuclear industrial application. Notably, these results proved that the formula of the emulsified suspension is not immutable, which is highly convenient for the actual operation of the system.

3.3.3. Radioactive Ion Fixation

The waste TBP/OK solvent was generated from PUREX. This ash inevitably contains some radioactive ions. It is necessary to reduce these radioactive ion emissions as much as possible. This project added nonradioactive Cs and Sr to simulate the 137Cs and 90Sr in waste TBP/OK solvent. The concentration of these ions was about 1 g/L. The results of these nuclide experiments of 30% TBP with Ca(OH)₂ are shown in Table 5.

Table 5. Nuclide simulation experiments of waste TBP/OK solvent with different emulsified suspensions.

Nuclide	C _{initial} (mg/kg)	C _{1-scrubber} (mg/kg)	C _{2-scrubber} (mg/kg)
Cs ⁺	842.22	\	\
Sr ²⁺	848.19	0.12	0.04

As shown in Table 5, Cs⁺ was not detected in the scrubber 1 or scrubber 2 because the phosphate [26] and pyrophosphate [27] in pyrolysis ash has excellent Cs⁺ adsorption abil-ities. The high-temperature gas filter (between the pyrolysis and the combustion furnace) could remove most of these nuclides. For Sr²⁺, only 0.04 mg/kg was detected in the scrub-ber 2. This is a low level concentration, which indicates that at least 99.995% of the nu-clides were fixed in this pyrolysis incineration system.

4. Conclusions

A large-scale pyrolysis incineration system for waste TBP/OK solvent, which consisted of a suspension preparation system (SPS), a pyrolysis and ash discharge system (PADS), and a combustion furnace and gas treatment system (CGS), was built. The suspension preparation system (SPS) system achieved the automatic preparation and feeding of emulsified suspensions. The feeding capacity could reach 30 kg/h. The pyrolysis and ash discharge system (PADS) decomposed the TBP/OK emulsified suspensions and rap-idly removed the pyrolysis ash. The combustion furnace and gas treatment system (CGS) burned pyrolysis gas without diesel oil and purified the generated products. The compat-ibility between multiple systems of this new design was verified. The pyrolysis ratio of the TBP/OK solvent was higher than 99.99%, while the phosphorus fixation ratio could reach 99%. This system fixed more than 99.995% of the radioactive nuclides. All these experi-mental results show that this pyrolysis incineration system is economically feasible and environmentally friendly, giving it a significant practical application value in the nuclear industry.

Author Contributions: Conceptualization, J.M.; methodology, J.M. and J.Z. (Jingyu Zhao); validation, J.M., T.L. and J.Z. (Jingyu Zhao); formal analysis, C.Y.; investigation, Y.W.; data curation, J.Z. (Jingyu Zhao); writing—original draft preparation, J.Z. (Jingyu Zhao); writing—review and editing, J.M., J.Z. (Jinghui Zhang), Y.S. and M.L. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: No new data were created or analyzed in this study. Data sharing is not applicable to this article.

Acknowledgments: The authors are grateful for the financial support from the China Nuclear Power Engineering Co., Ltd., China National Nuclear Corporation, Beijing, China.

Conflicts of Interest: The authors declare no conflict of interest.

References

- 1. Hee-Chul, Y.; Min-Woo, L.; Jei-Kwon, M.; Dong-Yong, C. Optimization of low-temperature pyrolysis process equipped with a two-stage non-flame oxidation system for the treatment uranium-bearing spent TBP. *Chem. Eng. Process.* **2015**, *94*, 11–19.
- 2. Yang, G.; Weifang, Z.; Xiaoming, C.; Shaolei, C. Influence of alpha and gamma radiolysis on Pu retention in the solvent TBP/kerosene. *Nukleonika* **2014**, *59*, 123–128.
- 3. Murali, M.; Mathur, J. Use of a mixture of TRPO and TBP for the partitioning of actinides from high-level waste solutions of PUREX origin and its comparison with CMPO and other phosphorus based extractants. *Solvent Extr. Ion Exch.* 2001, 19, 61–77. [CrossRef]
- Teng, D.; Shuibo, X.; Jingsong, W. Solidification and Stabilization of Spent TBP/OK Organic Liquids in a Phosphate Acid-Based Geopolymer. Sci. Technol. Nucl. Install. 2020, 2020, 8094205.
- 5. Kil-Jeong, K.; Jong-sik, S.; Woo-Seog, R. A practical method for the disposal of radioactive organic waste. *Nucl. Eng. Technol.* 2007, 39, 731–736.
- Masaki, O.; Yoshikazu, K.; Kazunori, N.; Yasumasa, T. Separation of actinides and fission products in high-level liquid wastes by the improved TRUEX process. J. Alloys Compd. 1998, 271, 538–543.
- Eddie, J.; Michael, J.; Danny, F.; Chris, J.; David, A. Recent Developments in the Purex Process for Nuclear Fuel Reprocessing: Complexant Based Stripping for Uranium/Plutonium Separation. *Chem. Mater. Nucl. Power Prod.* 2005, 59, 898–904.
- 8. Paiva, P.; Malik, P. Recent advances in the chemistry of solvent extraction applied to the reprocessing of spent nuclear fuels and radioactive wastes. *J. Radioanal. Nucl. Chem.* **2004**, *261*, 485–496. [CrossRef]
- 9. Dezhen, C.; Lijie, Y.; Huan, W.; Pinjing, H. Pyrolysis technologies for municipal solid waste: A review. *Waste Manag.* 2014, *34*, 2466–2486.

- 10. Wang, H.W.; Chen, M.Q.; Fu, K.; Wei, S.H.; Zhong, X.B. Evaluation on migration and transformation of trace nuclides in thermal degradation for low-level radioactive waste. *J. Anal. Appl. Pyrolysis* **2022**, *161*, 105420. [CrossRef]
- 11. Julia, T.; Troy, G.; Richard, B.; Jack, L. Development of Steam Reforming for the Solidification of the Cesium and Strontium Separations Product from Advanced Aqueous Reprocessing of Spent Nuclear Fuel. *Sep. Sci. Technol.* **2006**, *41*, 2147–2162.
- 12. Xu, T.; Wang, S.; Li, Y.; Li, J.; Cai, J.; Zhang, Y.; Xu, D.; Zhang, J. Review of the destruction of organic radioactive wastes by supercritical water oxidation. *Sci. Total Environ.* **2021**, *799*, 149396. [CrossRef] [PubMed]
- 13. Wang, S.; Qin, Q.; Chen, K.; Xia, X.B.; Ma, H.J.; Qiao, Y.B.; He, L.B. Supercritical water oxidation of spent extraction solvent simulants. *Nucl. Sci. Tech.* 2015, *26*, 030601.
- 14. Yan Jun, H.; Jing, J.; Gui Yin, G.; Fan, Z.; Xin Hua, L. A wet oxidation procedure of radioactive waste resin and waste concentrated liquid for 3H and 14C analysis. *J. Radioanal. Nucl. Chem.* **2020**, *326*, 765–771.
- 15. Fabiano, B.; Pastorino, R.; Ferrando, M. Distillation of radioactive liquid organic waste for subsequent wet oxidation. *J. Hazard. Mater.* **1998**, *57*, 105–125. [CrossRef]
- Lazareva, S.; Ismagilov, Z.; Kuznetsov, V.; Shikina, N.; Kerzhentsev, M. Uranium oxide catalysts: Environmental applications for treatment of chlorinated organic waste from nuclear industry. *Environ. Technol.* 2019, 40, 1881–1889. [CrossRef]
- 17. Ismagilov, Z.; Kerzhentsev, M.; Shkrabina, R.; Tsikoza, L. A role of catalysis for the destruction of waste from the nuclear industry. *Catal. Today* **2000**, *55*, 23–43. [CrossRef]
- Jouhara, H.; Nannou, T.; Anguilano, L.; Ghazal, H.; Spencer, N. Heat pipe based municipal waste treatment unit for home energy recovery. *Energy* 2017, 139, 1210–1230. [CrossRef]
- 19. Kuan, D.; Zhaoping, Z.; Daoxu, Z.; Bo, Z.; Xiaoxiao, Q. Pyrolysis of municipal solid waste in a fluidized bed for producing valuable pyrolytic oils. *Clean Technol. Environ. Policy* **2016**, *18*, 1111–1121.
- Miranda, R.; Pakdel, H.; Roy, C.; Vasile, C. Vacuum pyrolysis of commingled plastics containing PVC II. Product analysis. *Polym. Degrad. Stab.* 2001, 73, 47–67. [CrossRef]
- Miranda, R.; Jin, Y.; Christian, R.; Cornelia, V. Vacuum pyrolysis of PVC I. Kinetic study. *Polym. Degrad. Stab.* 1999, 64, 127–144. [CrossRef]
- Miranda, R.; Hooshang, P.; Christian, R.; Hans, D.; Cornelia, V. Vacuum pyrolysis of PVCII: Product analysis. *Polym. Degrad. Stab.* 1999, 66, 107–125. [CrossRef]
- 23. Hansen, J.; Deckers, J. Pyrolysis of Radioactive Spent Resins in the PRIME Installation. *Mater. Sci. Eng.* 2020, 818, 012008. [CrossRef]
- Xu, L.; Zhang, X.; Zhao, L.; Xue, P. The improvement and cold commissioning verification of a pyrolysis incinerating facility for Spent TBP/OK. *Radiat. Prot.* 2020, 40, 372–378.
- Zhang, C.; Gan, X.; Lin, M.; Wei, F.; Fan, X. Compound of Feed for Pyrolysis and combustion Spent TBP/Kerosene. At. Energy Sci. Technol. 2004, 38, 179–184.
- Natsumi, N.; Yoshikazu, K.; Takao, O. Immobilization of cesium by zirconium phosphate. J. Radioanal. Nucl. Chem. 2015, 304, 683–691.
- Fengli, S.; Zhe, S.; Huibo, L.; Haifeng, C.; Dan, L.; Cansheng, L.; Xiaorong, W.; Guoan, Y. Discussion on Adsorption Mechanism of Cesium by Zirconyl Pyrophosphate Compound. J. Nucl. Radiochem. 2014, 36, 186–192.

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.