# **Decomposition of Dibutyl Phosphate by Discharge inside Bubble in Water**

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Abstract: Decomposition of dibutyl phosphate dissolved in electrolyte solutions using discharges inside bubble is investigated. The concentration of dibutyl phosphate decreased by discharge inside the bubble in any solutions. Dibutyl phosphate is decomposed by a quasi-first order reaction of rate constants on order of  $10^{-5} \sim 10^{-4}$  s<sup>-1</sup> with input power of  $0.7 \sim 2$  W.

Keywords: Atmospheric plasma, Water treatment, Dibutyl phosphate, Nuclear reprocessing

## 1. Introduction

Reprocessing of spent fuel from nuclear power plant enables effective utilization of nuclear fuel, such as reuse of fuel material and reduction of waste volume [1]. Spent fuel contains residual uranium (U), newly produced plutonium (Pu), and high-level radioactive waste. The reprocessing process can separate uranium and plutonium from spent fuel. Generally, the PUREX process has been used to reprocess spent nuclear fuel in the nuclear fuel cycle [2], [3]. In the PUREX process, tributyl phosphate (TBP) is used as an extraction solvent for U and Pu [4]. TBP is degraded to dibutyl phosphate (DBP) by radiation ray in the solution [5]. DBP forms a complex with metal components in high level liquid waste (HLLW) and causes blockage in pipes [6], which leads unstable operation of reprocessing plants. Therefore, effective methods for DBP decomposition are required.

Discharge inside bubble in water treatment has attracted attention as a promising method for water treatment. A pulsed discharge inside bubble in water can produce chemical active species such as hydroxyl radical (•OH) and ozone (O<sub>3</sub>) at high density. Owing to their high oxidizing power, they contribute to decomposition of organic compounds without selectivity in a short time [7], [8]. This process realizes high-speed wastewater treatment without pretreatment, such as pH adjustment. This process also has the advantage that the chemically active species produced can be controlled by selecting the gas injected [9].

In this study, decomposition of DBP dissolved in alkaline solutions using discharges generated inside bubble is investigated. Three types of simulated alkaline solutions with different conductivities and ion contents were prepared. Conductivity of solutions is high as approximately 100 mS/cm. In the treatment of high conductivity solutions, discharge current becomes large because of low resistance of the solutions [9]. Thus, a capacitor is connected in series between the reactor and the pulsed power generator to suppress the conductive current flows into solution with high conductivity.

Table	1.	Sc	olute	es a	inc	l c	ond	luc	tivity
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of each simulated solution.						
Name	Solutes	Conductivity [mS/cm]				
DBP	DBP(23.8 mM) + NaOH(1M)	1.2				
SE1	DBP(23.8 mM) + NaNO <sub>3</sub> (1M) + Na <sub>2</sub> CO <sub>3</sub> (1M)	93				
SE2	$\frac{\text{DBP}(23.8 \text{ mM}) +}{\text{NaNO}_3(1M) +} \\ \frac{\text{Na2CO}_3(1M) +}{\text{NaNO}_2(1M)}$	117				



Fig. 1. Schematic diagram of the discharge reactor.



Fig. 2. Schematic diagram of the Magnetic Pulse Compression Circuit.

## 2. Experimental Setup

Three types of simulated alkaline solutions, DBP solution, SE1 and SE2, were prepared. Table 1 shows solutes and conductivity of each simulated solutions. DBP solution was prepared by dissolving sodium hydroxide



Fig. 3. Typical waveforms of the applied voltage and the current flowing on the reactor when DBP solution, SE1, and SE2 treatment.

(NaOH) and dibutyl phosphate. SE1 was prepared by dissolving sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>), sodium nitrate (NaNO<sub>3</sub>), and DBP. SE2 was prepared by adding sodium nitrite (NaNO<sub>2</sub>) to SE1. The concentration of NaOH, Na<sub>2</sub>CO<sub>3</sub>, and NaNO<sub>2</sub> was 1 M in each solution. The initial concentration of DBP

was 23.8 mM in each solution. The initial conductivities of DBP solution, SE1 and SE2 were 1.2, 93 and 117 mS/cm.

Figure 1 shows a schematic diagram of the discharge reactor. A tungsten wire is inserted into a glass tube and used as a high voltage electrode. Argon (Ar) gas is injected into the glass tube at a gas flow rate of 100 mL/min to generate bubble at the tip of the glass tube. The reactor is immersed in a water bath (LBT-400a, AS ONE Co.) up to a height of 40 mm from the bottom of the reactor to fix the solution temperature at 20 °C. Figure 2 shows a magnetic pulse compression circuit (MPC, Suematsu Electronics CO., LTD., MPC3000S SP) using to apply high voltage pules to the reactor. Peak value of applied voltage is 10 kV, and pulse repetition rate is 250 pps. A capacitor which has 50 pF capacitance is connected in series between the reactor and the pulsed power generator to suppress the conductive current flows into solution with high conductivity.



Fig. 4. The time course DBP concentration during discharge treatment.



Fig. 5. The time course energy efficiency for DBP decomposition during discharge

Figure 3 shows typical voltage–current waveforms of the pulse discharge inside bubbles in DBP solution. The peak applied value of reactor voltage( $v_r$ ) was fixed at 10 kV. Pulse width of  $v_r$  treating DBP solution, SE1, and SE2 are 100 ns, 50 ns, and 50ns, respectively. The consumed energy in the reactor per a pulse is calculated by integrating the electric power obtained by the output voltage and current over time. The energy of treating DBP solution, SE1, and SE2 are 8.5 mJ, 3.1 mJ, and 2.9 mJ, respectively.

#### **3.** Decomposition of Dibutyl Phosphate

Figure 4 shows the time course of DBP concentrations in DBP solution, SE1 and SE2 solutions during discharge treatment. The decomposition rates of DBP solution, SE1 and SE2 solutions after 9 hours treatment are 99%, 80% and 60%, respectively. The result indicates that discharge treatment is effective in DBP decomposition even in solutions containing NO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup> and NO<sub>2</sub><sup>-</sup>. DBP is decomposed by a quasi-first order reaction. The rate constants in the case of DBP solution, SE1 and SE2 are  $7.0 \times 10^{-5}$  s<sup>-1</sup>,  $3.6 \times 10^{-5}$  s<sup>-1</sup> and  $2.4 \times 10^{-5}$  s<sup>-1</sup>, respectively. Figure 5 shows energy efficiency for DBP decomposition as a function of treatment time. The energy efficiency for DBP decomposition decreases with increasing treatment time. The reaction rate between DBP and active species produced by discharges decreases with decreasing DBP



Fig. 6. The time course DBP, MBP, PO<sub>4</sub><sup>3-</sup>, and TOC concentration during discharge treatment.

concentration, and recombination loss reactions of active species increases, which leads decrease in the energy efficiency. The energy efficiency after 9 hours treatment in the case of DBP solution, SE1 and SE2 are 20 mol/Wh, 40 mol/Wh and 33mol/Wh, respectively. Energy efficiency is higher in the order of SE1, SE2 and DBP.

Figure 6 shows the time course of DBP, monobutyl phosphate(MBP), and phosphate( $PO_4^{3-}$ ) and total organic carbon (TOC) concentrations in the DBP solution during discharge treatment. MBP and  $PO_4^{3-}$  concentration increase to about 4 mM at 5 hours treatment.  $PO_4^{3-}$  concentration decreases with increasing treatment time. TOC concentration decreases with increasing treatment time. These results shows that DBP is decomposed to MBP and  $PO_4^{3-}$ , and 17 % of DBP is mineralized by 9 hours treatment. MBP concentration increases up to 5 hours treatment and then decreases. Active species generated by discharge preferentially react with DBP up to 5 hours.

#### 4. Conclusion

Three simulated DBP solution are treated by pulsed discharges inside bubbles in solution. DBP decomposition rate in case of DBP solution, SE1 and SE2, reaches 99%, 80% and 60%, respectively, after 9 hours treatment. DBP concentration decreases according to a quasi-first order reaction. The rate constants in the case of DBP solution, SE1 and SE2 are  $1.9 \times 10^{-4}$  s<sup>-1</sup>,  $4.8 \times 10^{-5}$  s<sup>-1</sup> and  $2.6 \times 10^{-5}$  s<sup>-1</sup>, respectively. DBP decomposed in solutions even containing NO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup> and NO<sub>2</sub><sup>-</sup>.

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