

## Ozone Oxidation Process for the Mineralization of Solvent Degradation Product-Di-N-Butyl Phosphate

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### Abstract

An experimental study using semi-batch reaction vessel to evaluate the applicability of ozone oxidation process for the mineralization of di-n-butyl phosphate, which is one of the major degradation product of PUREX solvent (Tri-n-Butyl phosphate). Power law kinetic model for prediction of the conversion profiles of DBP fitted with the experimental results well. From the analysis of experimental data it is found that first - order kinetic is appropriate to describe the oxidation kinetics of DBP. The influence of temperature and the combined effect of ozone on the oxidation efficiency of DBP have been carried out. The global reaction rate constants are found to be in the range of 10-3 min<sup>-1</sup>.

**Keywords:** PUREX process; Di-n-butyl phosphate; Ozone; Oxidation; Waste treatment; Fuel reprocessing; Spent solvent; TBP.



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### 1. Introduction

Tri-n-butyl phosphate (TBP) mixed with hydrocarbon diluents such as normal dodecane (nDD) are used in PUREX [1] process of nuclear fuel reprocessing plants. The organic solvents are radiolitically and chemically degraded during the process. The degradation products such as di-n-butyl phosphate (DBP) and mono-n-butyl phosphate (MBP), of which concentration are very low, reduce both solvent extraction efficiency of U and Pu and decontamination factors of fission products in solvent extraction steps [2]. Mainly acidic degradation products such as DBP and MBP are considerably removed from degraded solvents by using alkaline solutions at solvent washing step for reuse. However, the concentrations of degradation products retained in degraded solvents increase with recycle use. The degraded solvents come to be unsuitable for reuse and are discharged as spent solvents from the plant. The spent solvents consist of non-degraded TBP, non - degraded diluents and a small amount of degradation products. So the recovery of non-degraded TBP and diluents from the spent solvent is effective to reduce the volume of the organic waste. Distillation techniques have been developed for this purpose [3]. However, the organic residues which consist of TBP and degradation products having high boiling temperature are generated in distillation process of spent solvents. Waste treatments in NUCEF facility with silver mediated electrochemical oxidation technique have been carried out in France [4], United Kingdom [5] and United states [6]. The process such as acid digestion [7], pyrolysis [8] and ordinary incineration [9] which allows mineralization and volume reduction of the spent solvents including the distillation residues have been developed for the very long term storage. Destruction of dissolved tri-n-butyl phosphate (TBP) in simulated raffinate stream of nuclear fuel reprocessing has been studied in a semi-batch reaction vessel to confirm the destruction efficiency of TBP by ozone [10]. Alkaline hydrolysis process was developed for treatment and disposal of PUREX solvent waste [11]. Michael J. Watts and Karl G. Linden had carried out the efficacy of advanced oxidation processes for degrading trialkyl phosphate esters in treated source waters [12]. Use of Ozone and related oxidants for providing solutions for emerging pollutants of concern to the water and the environment had been discussed in international conference which was held in Geneva, Switzerland [13]. Ozonation process was tested for removal of dimethyl disulphide, dichlofenac, caffeine, levofloxacin and some pharmaceutical compound like ranitidine [14]. However the following disadvantages was noticed in each process. As to acid digestion, very corrosive reagents such as concentrated nitric acid and sulfuric acid mixtures are used at 500-600K to decompose TBP and degradation products. The material suitable for decomposition reactor is limited for the corrosive problem. As to pyrolysis, the spent solvents are pyrolysis with calcium hydroxide, which are added to neutralize decomposition products of TBP such as phosphoric acid for prevention of corrosion of reactor materials. As a result, a large amount of solid powders of calcium phosphate are produced at about 700 to 900 K. Concerning ordinary incineration process, a complicated off-gas treatment system of scrubber and filter is required to remove combustion products such as soot, phosphoric acid mist and radioactive aerosols. The high temperature incineration off-gas containing phosphoric acid mist and soot makes corrosion and sometimes causes the plugging of the off-gas piping. Alkaline hydrolysis process generates large volume of secondary waste. Wet oxidation using hydrogen peroxide process consumes high hydrogen peroxide and producing phosphoric acid waste. Oxidation using ozone

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will produce aqueous soluble secondary waste that could be immobilized in cement matrices. In this study, ozone oxidation techniques for mineralization of solvent (TBP) degradation products have been followed for the treatment of organic waste into stable form is desirable as a long-term strategy for the management of organic waste. An experimental study using a semi-batch reaction vessel to evaluate the applicability of ozone oxidation process for mineralization of solvent major degradation product DBP was conducted and realized.

## 2. Materials and Methods

### 2.1. Reagents

AR grades Sodium carbonate (anhydrous), Sodium hydrogen carbonates were used to prepare mobile phase solution for Ion-chromatography system. Sulfuric acid (AR grade) and ultrapure water were used to prepare the solutions for suppressed conductivity detection of Ion-chromatography system. Tri-n-butyl phosphate (> 98% pure), Di-n-butyl phosphate (> 98% pure) and nDD (> 99% pure) were used for the preparation of simulated solution to conduct the experiments. AR grade potassium iodide was used for the preparation of solution to kill the unreacted ozone comes out during the experimental runs. Mobile phase solution was filtered through a 0.45  $\mu\text{m}$  nylon membrane filter. Ultrapure water (18.2 Mega Ohm) was used for all solution preparations.

### 2.2. Instrumentation

A ozone generator made from ozonetek (Model no. AES01) with production capacity of 10 g ozone per hour was used. Oxygen gas was employed as feed gas for the generation of ozone. For the analysis of DBP, Metrohm-make modular Ion Chromatography system equipped with, 819 IC detectors, 820 IC separation center, 818 IC pump (Isocratic), 833 IC liquid handling unit and 830 IC interface were used. Sample was injected through a 20  $\mu\text{l}$  PEEK loop fitted with injector. IC net 2.3 Metrohm software was used for instrument control and data acquisition. Ion-chromatography column, Metrosep A Supp 5-250, 250 mL X 4.0 mm ID with Guard column Metrosep A Supp 4/5 were used for separation of components. 3.2mM  $\text{Na}_2\text{CO}_3$  + 1.0mM  $\text{NaHCO}_3$  with a flow rate of 0.7 ml/min was used as eluent.

## 3. Procedure

Simulated solution for conducting the experiments was prepared by adding known amount of DBP into 30% TBP-nDD solution, then known volume of this organic solution was taken in a 1000 ml capacity separating funnel and further mixed with 1% sodium carbonate. Aqueous phase was separated and known volume of aqueous solution was taken into semi-batch ozone reaction vessel, then ozone gas was purged through the frit and allowed to react with DBP. Unreacted ozone gas was allowed to react by passing through KI solution. Experiments were conducted by changing of solution temperatures from 25 to 30  $^{\circ}\text{C}$ . Samples were drawn at regular intervals to determine the DBP concentration by IC.

### 3.1. Analysis of DBP by Ion- Chromatography System

DBP analysis was carried out by taking known volume of aliquot from ozone reaction vessel, transferred into 10 ml standard flask and then made up to the mark with high purity milli Q water. Aqueous phase was injected into IC through 20  $\mu\text{l}$  PEEK loop and subsequent ion-exchange separations in anionic column, Ion-Chromatograms were obtained. A calibration graph for DBP in the concentration range of 1-50 ppm was made by preparing appropriate working standards of DBP solution in the mobile phase and analyzed directly in IC. Using this calibration graph concentration of DBP present in the unknown solution was calculated.

## 4. Results and Discussion

Fig.1 refers the calibration graph made for DBP concentration in the range of 1-50 ppm prepared in mobile phase with correlation coefficient 0.99974 and RSD 0.82%. This calibration graph is linear and used for the determination of concentration of DBP present in the unknown solution. Fig. 2 refers the typical ion chromatogram obtained before the oxidation of DBP by Ozone. DBP peak was eluted around 11 minutes under the identical chromatographic conditions. Fig.3 shows the typical ion chromatogram after the oxidation of DBP by Ozone. Fig.2 and 3 have clearly shown that quantitative oxidation of DBP is feasible after the extraction of DBP into alkaline medium and then subsequent treatment by using strong oxidant like ozone. Ozone can oxidise all compounds to their highest oxidation state if allowed to reach equilibrium. Thus, the following general theoretical reaction should occur:



Advantages of present technique are not only reducing the waste management load but also free from any addition of chemicals or needs for any further treatment. Fig.4 shows the effect of ozone oxidation at ambient temperature and the results obtained have confirmed that DBP initial feed concentration (2300 ppm) was reduced to DBP final concentration (30 ppm) within 600 minutes by treatment with ozone. Results of effect of temperature on the oxidation behaviour of DBP by ozone are shown in Fig.5. It was observed from the experimental data that time taken for the oxidation of almost all the DBP at ambient temperature is found to be slower than at elevated temperature. Power law kinetic model for prediction of the conversion profiles of DBP fitted the experimental results well. From the analysis of experimental data it is found that first - order kinetic is appropriate to describe the

oxidation kinetics of DBP in alkaline medium. The global reaction rate constants are found to be in the range of  $10^{-3} \text{ min}^{-1}$ .

## 5. Conclusion

Feasibility study was conducted to evaluate the applicability of ozone oxidation process for the mineralization of solvent degradation product waste generated in the PUREX process of nuclear fuel reprocessing plants. The influences of combined effect of ozone and temperature on the oxidation efficiency of DBP have been evaluated. Based on the experimental data, a new treatment process of spent solvent was proposed.

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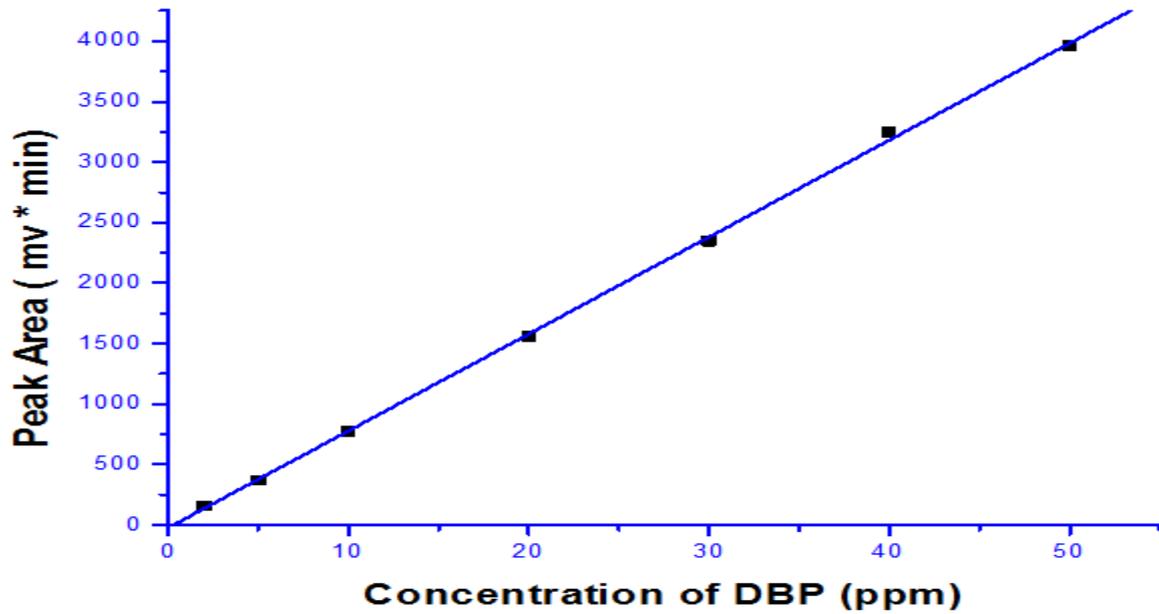
## Abbreviations

TBP: Tri-n-Butyl Phosphate  
 DBP: Di-n-Butyl Phosphate  
 nDD: Normal Dodecane  
 PUREX: Plutonium Uranium Refining by Extraction  
 MBP: Mono Butyl Phosphate  
 NUCEF: Nuclear Fuel Cycle Safety Engineering Research Facility  
 PEEK: Polyether ether ketone  
 IGCAR: Indira Gandhi Centre for Atomic Research  
 PEMS: Process Engineering and Modeling Section  
 RRDD: Reprocessing Research and Development Division  
 RpG: Reprocessing Group  
 IC: Ion-chromatography

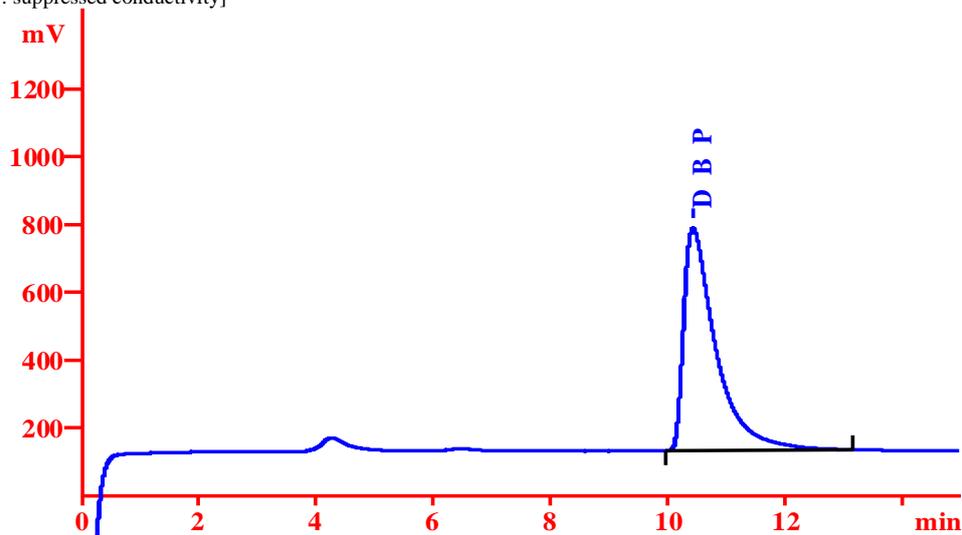
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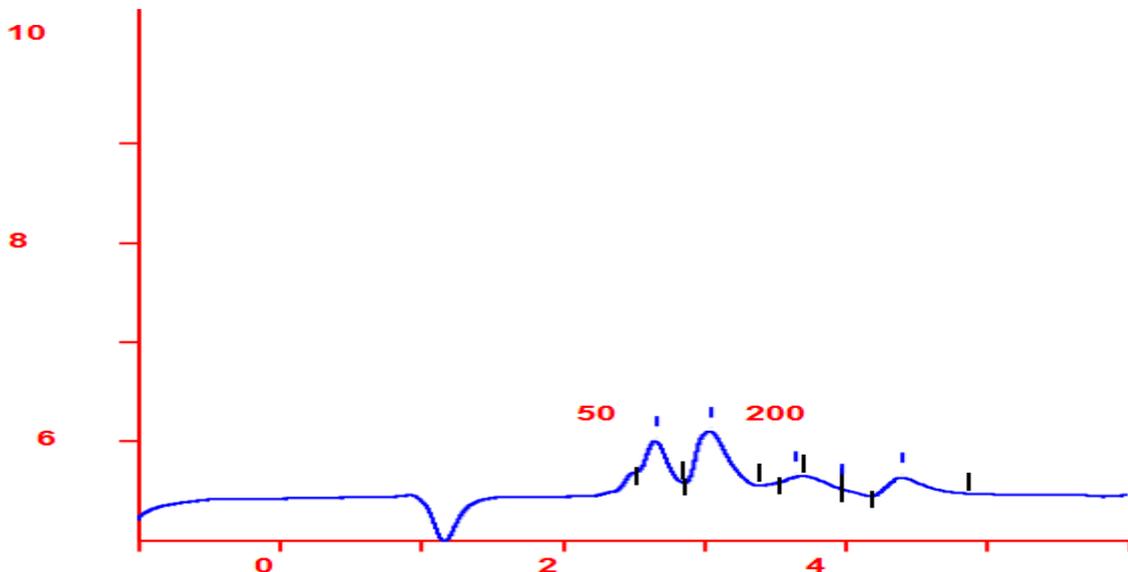
**Fig-1.** Typical calibration graph for the determination of DBP by Ion-Chromatographic technique. (DBP 1-50 ppm), [Column: Metrosep A Supp 5-250: [250 mm (L) X 4.0 mm (ID)]. Guard column: Metrosep A Supp 4/5, Eluent: 3.2 mM Na<sub>2</sub>CO<sub>3</sub>+ 1.0 mM NaHCO<sub>3</sub>, Flow rate: 0.7 mL/min, Injection volume: 20µl, Pump: isocratic, Detector: suppressed conductivity]



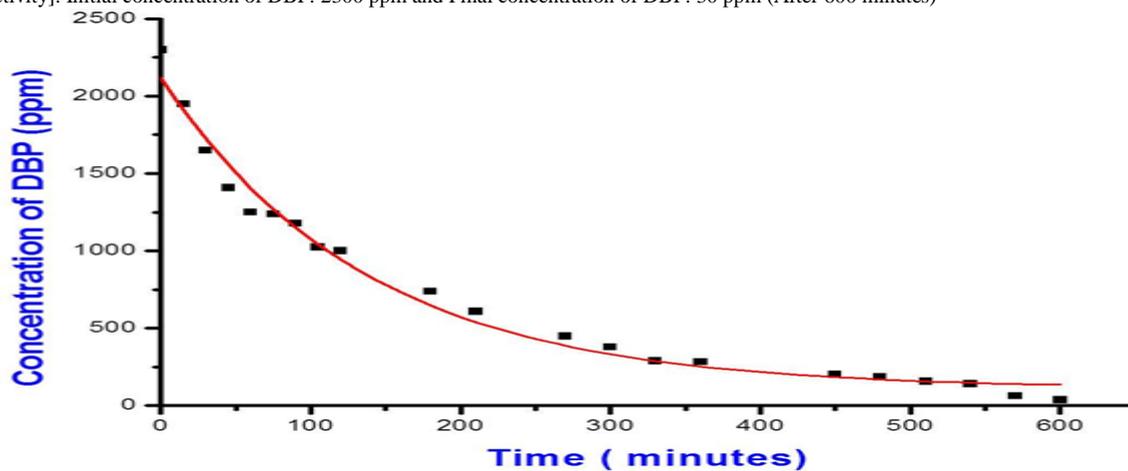
**Fig-2.** Typical ion chromatogram before oxidation of DBP (Initial concentration: 2300 ppm). [Column: Metrosep A Supp 5-250: [250 mm (L) X 4.0 mm (ID)]. Guard column: Metrosep A Supp 4/5, Eluent: 3.2 mM Na<sub>2</sub>CO<sub>3</sub>+ 1.0 mM NaHCO<sub>3</sub>, Flow rate: 0.7 mL/min, Injection volume: 20µl, Pump: isocratic, Detector: suppressed conductivity]



**Fig-3.** Typical ion chromatogram after oxidation of DBP [Column: Metrosep A Supp 5-250: [250 mm (L) X 4.0 mm (ID)]. Guard column: Metrosep A Supp 4/5, Eluent: 3.2 mM Na<sub>2</sub>CO<sub>3</sub>+ 1.0 mM NaHCO<sub>3</sub>, Flow rate: 0.7 mL/min, Injection volume: 20µl, Pump: isocratic, Detector: suppressed conductivity]. Concentration of DBP: 30 ppm



**Fig-4.** Extended oxidation of DBP by ozone at 25° C [Column: Metrosep A Supp 5-250: [250 mm (L) X 4.0 mm (ID)]. Guard column: Metrosep A Supp 4/5, Eluent: 3.2 mM Na<sub>2</sub>CO<sub>3</sub>+ 1.0 mM NaHCO<sub>3</sub>, Flow rate: 0.7 mL/min, Injection volume: 20µl, Pump: isocratic, Detector: suppressed conductivity]. Initial concentration of DBP: 2300 ppm and Final concentration of DBP: 30 ppm (After 600 minutes)



**Fig-5.** Effect of temperature on the oxidation of DBP by ozone [Column: Metrosep A Supp 5-250: [250 mm (L) X 4.0 mm (ID)]. Guard column: Metrosep A Supp 4/5, Eluent: 3.2 mM Na<sub>2</sub>CO<sub>3</sub>+ 1.0 mM NaHCO<sub>3</sub>, Flow rate: 0.7 mL/min, Injection volume: 20µl, Pump: isocratic, Detector: suppressed conductivity]

