Development and Demonstration of Vacuum Distillation Process for Recovery of Pure TBP and n-Dodecane from Simulated Organic Liquid Waste

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A mixture of Tri-butyl phosphate (TBP) and n-Dodecane used in nuclear fuel reprocessing plants have limited life because of formation of degradation compounds due to irradiation and chemical attack, leading to generation of spent solvent as radioactive organic Liquid Waste (OLW). To meet the objective of waste minimisation in high throughput plants, it is vital to develop a technology to recover and reuse of solvents from organic waste. Vacuum Distillation is envisaged as an effective method for removal of these degradation compounds and recovery of pure TBP & n-Dodecane from the organic waste. Careful design of Vacuum distillation system is very crucial as TBP is not highly volatile, a thermo-sensitive compound at elevated temperatures and having very low concentrations of variety of impurities in organic waste that need to be removed.

A plant scale vacuum distillation demonstration facility has been developed, designed and installed at TWMP, NRB, BARC, Tarapur. Successful trials have been carried out with simulated organic waste with recovery of significant portion of high purity TBP and n-Dodecane. The developed distillation system has an assured potential to become a standard and efficient treatment system in every radioactive organic liquid waste management plants in India.

Introduction

Nuclear fuel reprocessing plants use mixture of 30% TBP and 70% n-Dodecane (diluent) as solvent in PUREX process for extraction of heavy metals. This solvent after repeated use gets degraded mainly due to irradiation and chemical attack. This spent solvent is discarded which contains degradation products such as Di-butyl Phosphate (DBP), High Molecular weight Phosphate (HMP), Mono-Butyl Phosphate (MBP) and various diluent degradation products (DDP) e.g. Nitro, Nitrilo compounds, carboxylic acid, alcohol along with radioactivity. In present reprocessing plants, the spent solvent is regenerated by scrubbing with sodium carbonate by which most of the radioactivity associated with DBP is removed. However, residual activity due to other degradation products cannot be removed. These degradation products progressively accumulate in the solvent with repeated recycling and their removal from the solvent is not well addressed. Vacuum Distillation process is a most suitable process for Recovery of pure organics from spent OLW.

With an aim to recover the solvents from the organic waste to reduce the radiological and chemical impact on environment, and to reuse of the recovered pure organics to cut down the operating cost of the reprocessing plants, a vacuum distillation system has been developed after intensive literature survey, i,2,3, lab studies, detailed process design and equipment selection. Based on the detailed design, a complete plant scale system has been fabricated, installed and commissioned at Tarapur site for demonstration trials. The developed Vacuum distillation has broadly two sections- 1) Evaporation in ATFE for removing major portion of HMP impurity and 2) Batch distillation with rectification in distillation column for recovering pure n-Dodecane and TBP as distillate cuts. During the trials with simulated waste, an effective recovery of TBP and n-Dodecane with purity greater than 99.9% was achieved. The quality of recovered organics is at par with fresh organic being used in reprocessing plants.

Process Description

Vacuum distillation plant is developed as per the process flow scheme shown in Figure-1. Organic waste is received in OLW receipt tank and subjected to washing by 0.5 M sodium carbonate to remove most of the DBP. After washing, organic waste is fed in continuous mode to Agitated Thin Film Evaporator-1 (ATFE-1) section, which is maintained at high vacuum and low temperature. LP steam is used for heating in evaporators. The vapours generated are condensed in a condensers utilizing chilled water. The condensate from ATFE-1 becomes free from major portion of high boiling impurities which remains as residue in the bottom of ATFE-1. Thereafter, a batch of organic condensate collected is transferred to kettle of batch distillation section comprising of Agitated Thin Film Evaporator-2 (ATFE-2) acting as a reboiler, distillation column with rectification section, condenser, reflux drum, etc. High vacuum and low temperature are maintained in ATFE-2. Vapours from ATFE-2 are fed to distillation column, which is operated to recover various distillate cuts like (i) n-Dodecane cut, (ii) impurities (DDP) cut and (iii) TBP cuts, from top of the column by adjusting temperature at ATFE-2. HMP and DBP-rich impurities are retained at bottom of kettle. The purified TBP and n-Dodecane are stored in separate vessels. An alkaline
wash is also provided to the recovered organic to eliminate traces of Di-Butyl Phosphoric acid which could be carried along by the TBP vapours.

For inactive trial runs in this plant, simulated organic waste was used. Simulated organic waste was prepared by equilibrating mixture of 30% TBP & 70% Dodecane with 4M Nitric Acid solution and irradiating the mixture by using gamma source in a radiation field of 1 X 105 R/hr. The irradiation duration was fixed to match the extent of degradation of simulated waste with actual organic waste.

The composition of simulated OLW & plant OLW are as follows:

**Equipment Selection**

As the TBP is not highly volatile and it is a thermo-sensitive compound, this distillation is carried out at low pressure and temperature by using two stage vacuum pump. To minimize the residence time of the fluid during evaporation in the heated zones, ATFE-1 & ATFE-2 are used. Vapours from ATFEs are condensed in shell and tube type condensers. For purification of TBP & Dodecane, a packed bed distillation column with very low pressure drop and high efficiency is used. 3-D view of the plant is shown in Fig.-2 and photographs of major equipment of this plant are shown in Figure-3 & 4. Alkaline washing tanks are provided for removal of DBP impurities at beginning and at the end of the process cycle.

Mechanical design of process equipment is carried out conforming to ASME Section VIII, Div.1. Material of Construction of all major equipment and associated piping is austenitic stainless steel grade 304L. Instrumentation and Control system has been adapted for monitoring and controlling of process parameters like level, temperature, pressure and flow. Sizing of each equipment & piping has been

<table>
<thead>
<tr>
<th>Table 1: Composition of simulated OLW &amp; plant OLW</th>
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<tbody>
<tr>
<td><strong>Description</strong></td>
</tr>
<tr>
<td>Simulated OLW</td>
</tr>
<tr>
<td>Plant OLW</td>
</tr>
</tbody>
</table>
arrived for system design capacity of 40 LPH (32 KGPH) feed rate of organic waste.

**Laboratory Scale Studies**

For design of distillation column, it is imperative to know vapour-liquid equilibrium (VLE) behaviour of TBP and n-Dodecane with respect to major impurities present in organic waste. Various laboratory experiments were conducted at different temperatures and concentrations of TBP, n-Dodecane and impurities. Typical lab results are given below:

These results were used for design of distillation column.

**Plant Scale Demonstration Trial Results**

The trial runs were carried out with simulated organic waste of about 500 litres (400 kg). After initial carbonate wash, simulated organic waste was fed to ATFE-1. Residue collected at bottom of ATFE-1 operation was maintained at 5-10%. The rest condensed top organics from ATFE-1 operation was transferred to Kettle of batch distillation column. Distillation column was operated in batch mode with rectification in packed bed by giving reflux at varying reflux ratios for different product cuts. Several trial runs were carried out with varying process parameters and samples of recovered n-Dodecane and TBP cuts were analysed by Gas Chromatographer at NRB/NRG Laboratories. The results are tabulated below:

a) **Gas Chromatography test results**

Table 2: Typical normalized VLE behaviour of Dodecane w.r.t. TBP

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Dodecane</th>
<th>TBP</th>
</tr>
</thead>
<tbody>
<tr>
<td>°C</td>
<td>% in liquid</td>
<td>% in liquid</td>
</tr>
<tr>
<td>75</td>
<td>45.69</td>
<td>54.31</td>
</tr>
<tr>
<td>90</td>
<td>50.58</td>
<td>49.42</td>
</tr>
</tbody>
</table>

Table 3: Typical normalized VLE behaviour of n-Dodecane w.r.t. DDP

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Dodecane</th>
<th>DDP</th>
</tr>
</thead>
<tbody>
<tr>
<td>°C</td>
<td>% in liquid</td>
<td>% in liquid</td>
</tr>
<tr>
<td>72</td>
<td>99.824</td>
<td>0.176</td>
</tr>
<tr>
<td>80</td>
<td>99.804</td>
<td>0.196</td>
</tr>
</tbody>
</table>

Table 4: Typical VLE behavior of TBP w.r.t. HMP

<table>
<thead>
<tr>
<th>Temperature</th>
<th>TBP</th>
<th>HMP</th>
</tr>
</thead>
<tbody>
<tr>
<td>°C</td>
<td>% in liquid</td>
<td>% in liquid</td>
</tr>
<tr>
<td>75</td>
<td>49.8</td>
<td>68.2</td>
</tr>
<tr>
<td>90</td>
<td>47.0</td>
<td>4.3</td>
</tr>
</tbody>
</table>

These results were used for design of distillation column.
Table-5: Gas Chromatography test results

<table>
<thead>
<tr>
<th>DESCRIPTION (STREAMS)</th>
<th>RECOVERED VOLUME</th>
<th>% RECOVERY</th>
<th>TBP PURITY</th>
<th>n-DODECANE PURITY</th>
<th>TECH. SPECS. PURITY FOR FRESH ORGANICS</th>
</tr>
</thead>
<tbody>
<tr>
<td>RECOVERED DODECANE</td>
<td>310 litres (233 kg)</td>
<td>85%</td>
<td>-</td>
<td>99.97%</td>
<td>98%</td>
</tr>
<tr>
<td>RECOVERED TBP</td>
<td>40 litres (39 kg)</td>
<td>30%</td>
<td>99.9%</td>
<td>-</td>
<td>99%</td>
</tr>
</tbody>
</table>

b) Uranium Loading & Stripping Test:

Recovered n-Dodecane & TBP was mixed in the ratio of 70:30 and tested for Uranium loading & stripping at reprocessing plant laboratory. The result shows that extent of uranium extraction is 100% and uranium stripped is 99.63%. Thus, U-retention is much less than the minimum required for recycle.

c) Pu retention Test:

Recovered n-Dodecane & TBP was mixed in the ratio of 70:30 and tested for Pu retention test at reprocessing plant laboratory. The extent of Pu retained in organic phase is negligible.

Based on the above test results, Reprocessing Plant Laboratories certified that the quality of vacuum distilled TBP & n-Dodecane is at par with fresh TBP & n-Dodecane.

Conclusion

The plant scale Vacuum Distillation System was successfully developed, designed, fabricated, installed and operated to demonstrate the recovery of Dodecane (85% by volume) with purity of 99.97% and TBP (30% volume) with purity of 99.9% from simulated OLW. The recovered organics quality is at par with fresh organics as certified by reprocessing plant laboratories and meets the specification for reuse in reprocessing plant. The recovery volume of 68.5% of pure solvent from degraded solvent has been achieved and volume of simulated OLW is reduced to 31.5% only. Further trial runs are planned to increase the recovery percentage by adjusting the process parameters.

Acknowledgement

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References


Abbreviations

TBP: Tri-n-butyl phosphate  
DBP: Di-butyl phosphate  
MBP: Mono butyl phosphate  
DDP: Diluent (n-dodecane) degradation products  
HMP: High molecular weight phosphates  
ATFE: Agitated thin film evaporator  
OLW: Organic liquid waste  
RP: Reprocessing plant