

# The Application Of Nitrogen Laser On Extraction Of Uranium In The Long Life Of High Level Radioactive Liquid Waste Using TBP-Kerosene Solvent

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## Abstract :

The radionuclide of uranium (U) is major radionuclide contained in the long life of high level radioactive liquid waste (HLLW) generated from reprocessing of spent nuclear fuel. The radioactive waste have to be treated to ready for long term disposal. Separation of the U at high efficiencies greatly lowers the volume of the long life alpha radioactive waste to be disposed and decreases the hazard level of the waste. The technology assessment of selective separation of U was carried-out as alternative and strategy for HLLW management in the future. The selective separation technology of U from fission products at very high efficiencies was developed by the extraction process using TBP-kerosene solvent and increasing the separation by exposure of nitrogen (N<sub>2</sub>) laser radiation at wavelength 337.1 nm. In the extraction process for simulation waste containing U and Zr in 5 M HNO<sub>3</sub> (Zr as one of fission product which difficult to be separated from U) using 30 % TBP-kerosene solvent and by exposure of nitrogen laser radiation shows that increasing of distribution coefficient of U (Kd U) can obtains 135 % and increasing of separation factor of U and Zr (SF<sub>(U/Zr)</sub>) is 189 %. The increasing of Kd U using N<sub>2</sub> laser higher than using CO<sub>2</sub> laser (at the wave-number 944 cm<sup>-1</sup>) which increase of Kd U only 100 %. In Indonesia, assessment for adaptation of the separation technology by extraction for separation of U process using 30 % TBP-kerosene solvent should be carried-out as alternative for treatment the HLLW generated from <sup>99</sup>Mo radioisotope production and from post irradiation examination of nuclear fuel.

**Keywords:** extraction, high level radioactive waste, photochemistry of laser, tributylphosphate, uranium.

## 1. Introduction

In Indonesia, Radioactive Waste Technology Center (RWTC) –National Nuclear Energy Agency of Indonesia (BATAN) responsible for research and development (R&D) and services in the field of radioactive waste management. Based on the responsible, the CRWT has a task to execute the treatment of radioactive waste generated from R&D and application of nuclear energy including radioactive waste from non nuclear industries in Indonesia. The application of radioactive waste management technology in accordance with regulation of the applicable safety standards to support the nuclear energy application program in Indonesia, it is aimed to ensure the safety for workers and the public, as well as to protect the environmental impacts from potential of radiation hazard for present and future generations.

The RWTC-BATAN has been steadily implementing the radioactive waste technology, especially for low level radioactive waste (LLW) and intermediate level radioactive waste (ILW) which have short half life ( $\leq 30$  years). Further to manage the long life of high level liquid radioactive waste (HLLW) and transuranium liquid radioactive waste (TRULW) generated from the utilization of nuclear energy, it is necessary to set up its processing technology both on the reduction of waste volume and waste immobilization process (solidification process) to become packaging waste (wasteform) to be able to survive for long-term storage (many million of years) in the disposal facility (Deep Geological Disposal Facility). The HLLW contains fission product elements and some long life alpha emitter radionuclides such as uranium (U), plutonium (Pu) and other actinides such as neptunium (Np), americium (Am), and curium (Cm). The radionuclides have very long half-life, i.e. : <sup>238</sup>U = 4,5x10<sup>9</sup> years, <sup>235</sup>U = 6,8x10<sup>8</sup> years, <sup>239</sup>Pu = 2,41x10<sup>4</sup> years, <sup>257</sup>Np = 2,1 x 10<sup>6</sup> years, <sup>243</sup>Am = 7,4x10<sup>3</sup> years, and <sup>241</sup>Am = 4,3x10<sup>2</sup> years [1].

In some countries which have reprocessing plant (closed fuel cycle strategy), the HLLW are generated from the first cycle extraction of the spent fuel reprocessing plant. Reprocessing of spent nuclear fuel is a process to recover the remaining uranium (U) and plutonium (Pu) elements in spent nuclear fuels. The HLLW contains fission product elements as major elements and transuranium elements as minor elements (as contaminants). In the second cycle extraction is generated transuranium liquid waste (TRULW) containing transuranium elements as major elements and fission product as minor elements. In the other hand, some countries which have open fuel cycle strategy (there is no reprocessing of spent nuclear fuel), such as Indonesia, the high level radioactive waste

(HLW) means the spent fuel it self. At present in Indonesia, spent nuclear fuels of research reactor as HLW are direct stored or re-exported (sent back) to the origin country of uranium supply namely from United State of America [2]. Whereas, the HLLW are generated from  $^{99}\text{Mo}$  radioisotope production (using uranium target) in Radioisotope Production Installation (RPI) and from post irradiation examination of nuclear fuel in Radiometallurgy Installation (RMI).

In the reprocessing of spent nuclear fuel, separation of uranium at the first step is carried-out by extraction process using organic solvent of 30 %TBP (tri-n-buthyl phosphate) in kerosene. There are some fission product elements which difficult to separate from uranium, i.e. :  $^{95}\text{Zr}$ ,  $^{141}\text{Ce}$ ,  $^{144}\text{Ce}$ ,  $^{103}\text{Ru}$ ,  $^{106}\text{Ru}$ , and  $^{131}\text{I}$ . The three radionuclide elements namely  $^{95}\text{Zr}$ ,  $^{103}\text{Ru}$ , and  $^{106}\text{Ru}$  are extremely difficult to be separated from uranium [3]. The three radionuclide elements follows together with uranium to be extracted into organic phase of TBP-kerosene. Separation of the uranium at high efficiencies greatly lowers the volume of the long life alpha radioactive waste to be disposed and decreases the hazard level of the waste. One of alternative to increase the separation factor of uranium from fission product elements is by addition of photochemistry process using laser radiation exposure on the extraction process. The technology assessment of selective separation of uranium was carried-out as alternative and strategy for treatment of HLLW in the future.

In this paper is presented the assessment of uranium separation process containing in the HLLW by solvent extraction using TBP-kerosene and the application of nitrogen laser radiation to increase distribution coefficient of uranium ( $K_d \text{ U}$ ) and its separation factor of uranium and zirconium,  $SF_{(\text{U/Zr})}$ . Zirconium (Zr) is one of fission product which difficult to be separated from uranium. This assessment aimed to adaptation the separation technology for uranium by extraction process using 30 % TBP-kerosene solvent should be carried-out as alternative for treatment the HLLW generated from  $^{99}\text{Mo}$  radioisotope production (in RPI) and from post irradiation examination of nuclear fuel (in RMI).

### Theory

The photochemistry process by laser radiation in the field of chemistry has been used for separation and chemical and biochemical synthesis. Whereas in nuclear chemistry, photochemistry by laser radiation have been used for isotope separation and the separation of nuclear isomerics [4]. Photochemistry can be carried-out by laser radiation in the region of infrared, visible, ultraviolet, or radiation with shorter wave-lengths. Photochemistry by infra-red laser radiation is photochemistry that stimulate chemical reactions through excitation of vibration energy level while the electronic energy levels are at its ground state energy level. Whereas photochemistry by visible and ultraviolet laser radiation is photochemistry that stimulate chemical reactions through excitation of electronic energy level. The general concept of chemical separation by photochemical processes by laser radiation is shown in Figure 1.

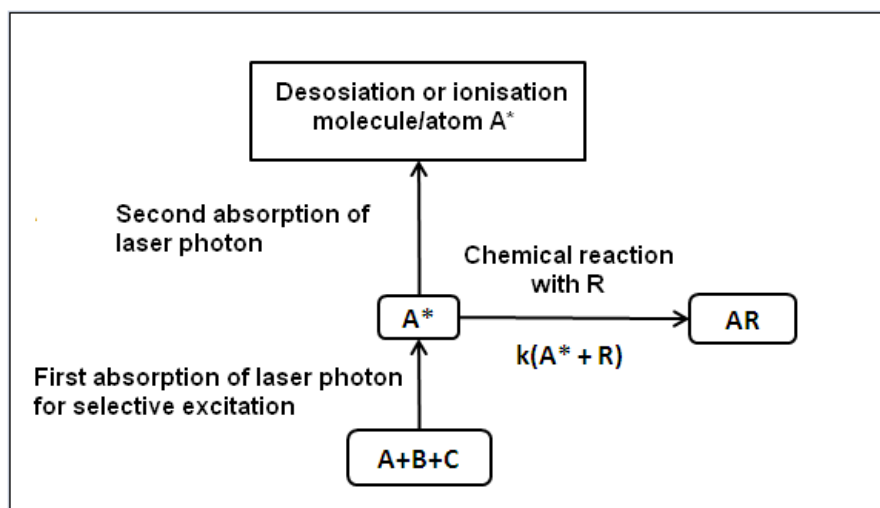


Figure 1. General scheme of the chemical separation by laser radiation excitation [5].

When a mixture of several particles A, B, C, and so on (in the form of atoms or molecules) having small or no different in its chemical properties, so separation of the particles will be very difficult and sometimes impossible to be separated by ordinary chemical methods, but due to the quantum levels of the particles are quite different,

therefore one of particle can be excited selectively by monochromatic laser radiation at selected characteristics wave-length, while the other particles are not excited. The excited particle is changed its chemical and physical properties, so it can be used for separation of particle (in the form of compounds) by several methods based on different excitation characteristics of the particles with the other particles are not excited.

Selective excitation of particle (molecule/atoms) A contained in mixture with particles of B and C, by laser radiation at the specific wave-lengths for excitation of particle A to become particle A\* (the excited particle A), further the chemical reaction of particle A\* with reagent R (atom/molecule) to produce AR, or by second absorption of laser photon so that the excited particle A\* will be occurred dissociation or ionization processes. Excitation energy is very higher than non selective thermal energy that can be accepted by the other particles at a lower energy level in the mixture. Based on the scheme in Figure 1, the chemical separation occurs through stages of process as follows [5] :

- (1). Selective photoexcitation of molecule/atom A by laser to become A\*.
- (2). Chemical reaction of the excited molecule/atom A\* with reagent R to become AR compound.
- (3). Isolation of AR compound by physical or chemical methods.

Process of (1) and (2) can be occurred very fast because the lifetime of excited molecule/atom A\* is very short between  $10^{-6}$  –  $10^{-9}$  seconds [6]. The process can be done if the process of irradiation by laser (photoexcitation process), the reagent of R has to be prepared in the same system together with particle of A, so that the capture process of excited molecule/atom A\* by reagent R to become AR occurs quickly before the excited molecule/atom A\* return to the ground-state energy level. From the process (2) is produced a stable compound of AR. The compound of AR can be easily separated from the system in the process (3) by physical or chemical methods. Based on the process, CO<sub>2</sub> laser radiation (infrared laser) and nitrogen (N<sub>2</sub>) laser (ultraviolet-visible laser) have been tried for increasing the separation of uranium from fission product elements.

## 2. Material and Methods

The assessment is carried-out based on study and analysis of data gathering from several publication related to the application of laser on extraction of uranium contained in the long life of HLLW using TBP-kerosene solvent. The assessment was started by studies and analyzes of the theory concerning the laser application in chemical separation, then it is studied and analyzed the treatment of HLLW including TRULW containing uranium and fission product elements, behavior of uranium and fission product elements in the extraction process using TBP-kerosene, and development of extraction process for separation of uranium by laser application (ultraviolet-visible and infrared lasers). Finally, the study and analysis are carried-out for the adaptation of the separation technology of uranium contained in the HLLW by extraction process using 30 % TBP-kerosene solvent. The adaptation of uranium separation technology is prepared as an alternative for treatment of the HLLW generated from 99Mo radioisotope production in RPI and from post irradiation examination of nuclear fuel in RMI.

## 3. Result and Discussion.

### 3.1. The Management of High Level Radioactive Liquid Waste

The nuclear fuel is unloaded from the reactor if its economical life has been reached, and then become spent nuclear fuel (SNF). The SNF still contains radionuclides (radioactive elements) i.e. : remaining U, Pu, TRU, and the fission product elements. The remaining U contains <sup>235</sup>U (fissile nuclides) and <sup>238</sup>U (fertile nuclides). Whereas Pu is the new nuclear fuel containing its isotopes i.e. : <sup>238</sup>Pu, <sup>239</sup>Pu, <sup>240</sup>Pu, <sup>241</sup>Pu, and <sup>242</sup>Pu producing from breeding reaction of <sup>238</sup>U with neutron. Radioisotope of <sup>239</sup>Pu is the main of new fissile material. The composition of nuclear fuel before and after use in Nuclear Power Plant is shown in Table 1.

**Table 1.** The composition of nuclear fuel before and after use (fresh fuel and spent fuel) in Nuclear Power Plant [7,8].

Nuclides	Fresh Fuel	Spent Fuel
<sup>238</sup> U (fertile nuclide)	95,5 %	93 %
<sup>235</sup> U (fissile nuclide)	4,5 %	1 %
Pu and TRU	-	1 % *)
Fission Products	-	5 %

\*) TRU (Np, Am, Cm) in small quantity lower than 0,1 %.

In some developed countries in the field of nuclear technology that implement to a closed fuel cycle strategy such as Japan, France, England, United State of America, India, and Pakistan, they do reprocessing of spent nuclear fuel to recover the remaining uranium and plutonium, then the uranium and plutonium are utilized for fabrication of new nuclear fuel assembly, namely mixture nuclear fuel  $UO_2$  and  $PuO_2$  (*mixture oxyde, MOX*) [2].

The HLLW from reprocessing plant are usually in the form of nitric acid liquid with high acidity about 6 – 8 N. The volume of HLLW is reduced by evaporation, and the concentrate of HLLW is immobilized through solidification process. The immobilization technology of HLLW by vitrification process has been operated industrially in many countries. At present, glass of borosilicate is utilized industrially for immobilization of HLLW. Besides that, development of immobilization technology by synroc is in progress. Synroc is titanate mineral that has high chemical resistant. Development of synroc technology in technical scale was carried out in Australia, United Kingdom, and Japan in collaboration with Australia. The block waste packages (wasteforms) resulted from the immobilization process are ready stored in the interim storage facility using cooling system for 30-50 years and further it are stored for long-term storage in the Deep Geological Disposal Facility [9].

Over the last 50 years in developed countries of nuclear such as United State of America, England, France, and Rusia, their nuclear defense activities have produced large quantities of nuclear waste (HLLW and TRULW) that now require disposal. Using conventional techniques, this process could cost billions of dollars at a site like Hannford alone. Disposal cost are based on the volume of materials treated, therefore, reducing the volume is a major cost savings opportunity and how to do that is a high technology priority. The radioactivity level is over 200 million curies. Pu, U, Am, Cs, and Sr are major contributors causing this to be HLW. Although they occur in comparatively small concentrations <sup>137</sup>Cs and <sup>90</sup>Sr contribute 98 % of the thermal energy and 97 % of the penetrating radiation from the waste during the first 30 years after the radioactive waste is formed [10]. The cost effective removal of those two elements greatly decreases the volume of waste to be converted to glass and sent to geological disposal and results in billions of dollars of savings. In the HLLW and TRULW, the content of Pu very lower than U namely about  $9.68 \times 10^{-3}$  according to the comparison in spent nuclear fuel (Table 1).

HLLW and TRULW containing long life alpha emitter radionuclides namely U, Pu, and the other actinides (TRU) such as Np, Am, and Cm. Beside that the waste always also containing fission products which difficult to be separated namely <sup>95</sup>Zr, <sup>103</sup>Ru, and <sup>106</sup>Ru. In the extraction process using 30 % TBP-kerosene, there are fission products which difficult to be separated from uranium namely <sup>95</sup>Zr, <sup>141</sup>Ce, <sup>144</sup>Ce, <sup>103</sup>Ru, <sup>106</sup>Ru, and <sup>131</sup>I. The fission product which seriously very difficult to be separated from uranium are only <sup>95</sup>Zr, <sup>103</sup>Ru, and <sup>106</sup>Ru, and they together with U are extracted into organic phase of TBP-kerosene [3].

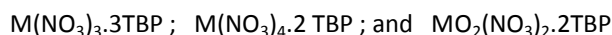
U and Pu are major contributors of the long life alpha emitter in the HLLW. Removing of the U (and Pu) from fission product elements contained in HLLW or TRULW at high efficiencies greatly lowers the volume of the long life alpha radioactive waste to be disposed and decreases the hazard level of the waste, and also to increase integrity of the waste block (waste form) producing from immobilization process, so that it can give a great saving of disposal cost [11].

The technology assessment of selective separation of U was carried-out as alternative and strategy for HLLW management in the future. The selective separation technology of U from fission products at very high efficiencies was developed by the extraction process using TBP-kerosene solvent and increasing the separation factor by exposure of nitrogen ( $N_2$ ) laser radiation at wavelength 337.1 nm. Application of laser radiation is one of alternative to increasing the separation factor of U (and Pu) from Zr and Ru elements.

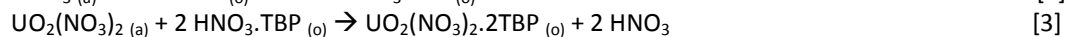
### 3.2. Behavior of Uranium and Fission Product Elements in the Extraction Process using TBP-Kerosene

Uranium, plutonium, and fission product elements can be extracted into the organic phase (TBP-kerosene) in the form of nitrate-complex compounds that bind some TBP molecules. In the extraction process system with

aqueous phase containing nitric acid (HNO<sub>3</sub>) and organic phase of TBP, the cations (M) will be extracted in the compound forms as follows [12] :



The cations of U, Pu, and fission product elements have empty electron orbitals in the energy levels of d and f, so that it can be the acceptor of electron pairs from oxygen atoms (as electron donor) in functional groups of TBP. In the extraction system, U will be extracted by the mechanism as follows [12,13] :



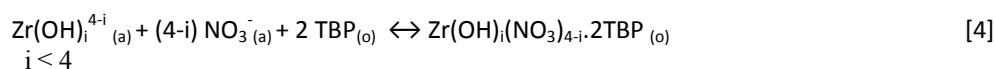
In these reactions, (a) and (o) are notations for aqueous phase and organic phase respectively. The value of distribution coefficient for U namely  $K_d U = [UO_2(NO_3)_2 \cdot 2TBP](o) / [UO_2^{++}](a)$ . Additional of NO<sub>3</sub><sup>-</sup> ion in aqueous phase will shift equilibrium to species which can be extracted namely UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>. In the reprocessing of spent nuclear fuel often is added the salts such as Al(NO<sub>3</sub>)<sub>3</sub> atau NH<sub>4</sub>NO<sub>3</sub> in the great quantity to increase K<sub>d</sub> U. These salts are called salting out agent. The extraction mechanism for fission product elements are similar with U, it is also in the forms of nitrate complex compounds. Fletcher [15] divides the nitrate complex compounds into three groups as shown in Table 2.

**Table 2.** The Grouping of Nitrate Complex compounds according to its coordination bonding strength with TBP [14,15].

No	Metal/Radical of Central Atom	Complex Form in TBP Solvent
1	Group - A (Strength) : UO <sub>2</sub> <sup>++</sup> , PuO <sub>2</sub> <sup>++</sup> Pu <sup>4+</sup> , U <sup>4+</sup> , Zr <sup>4+</sup> , Ce <sup>4+</sup> Ru(NO) <sup>3+</sup>	- Di and tri-nitrate complexes - Tetra and hexa-nitrate complexes - Tri-nitrate complexes
2	Group - B (Weak): Pu <sup>3+</sup> , I, Ce <sup>3+</sup> , La, Pr, Nb, and the other rare earth (RE).	- Tri-nitrate or the other of higher complexes.
3	Group -C (Very weak): Cs, Sr, Ba, Mo, Tc, Rh, dan Ru <sup>4+</sup> .	- Its quantity are very small and possibility of its species form are nitrate complexes.

In Table 2, it is shown that the greatest part of fission product elements will be able separated from U (and Pu), namely fission product elements included in group of B and C, but there are some fission product elements that are difficult to be separated from U included in the same group A, namely : Zr<sup>4+</sup>, Ce<sup>4+</sup>, and Ru(NO)<sup>3+</sup>. These radionuclides of fission product elements are <sup>95</sup>Zr, <sup>141</sup>Ce, <sup>144</sup>Ce, <sup>103</sup>Ru, dan <sup>106</sup>Ru. Besides that, the radionuclide of <sup>131</sup>I also become problem in the extraction process of U. This is due to the occurrence of iodination reaction on the alkyl chain of TBP, so that increase K<sub>d</sub> iodine. However as mentioned earlier that only <sup>95</sup>Zr, <sup>103</sup>Ru, and <sup>106</sup>Ru are seriously very difficult to be separated from uranium, and they together with U are extracted into organic phase of TBP-kerosene [3].

The extraction mechanism of Zr containing in HNO<sub>3</sub> solution by TBP has been reported by Egorov [17] that the mono or di-solvation formation of zirconium nitrate with TBP depends on concentration of the free solvent, although exactly that Zr is not competed with HNO<sub>3</sub> for formation of coordination bonds with TBP. The research shown that during the extraction process at the concentration range of HNO<sub>3</sub> 3-7 M, the first was monosolvation namely Zr(NO<sub>3</sub>)<sub>4</sub>TBP and then it was formed disolvation namely Zr(NO<sub>3</sub>)<sub>4</sub> 2TBP. According to Salovkin [17], zirconium in organic phase (TBP) has complex forms i.e : Zr(NO<sub>3</sub>)<sub>4</sub>·2TBP, Zr(OH)(NO<sub>3</sub>)<sub>3</sub>·2TBP, and Zr(OH)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·2TBP. Reaction mechanism of Zr generally on extraction with TBP is follows [16] :



The distribution coefficient of Zr,  $K_d Zr = [Zr(OH)_i(NO_3)_{4-i} \cdot 2TBP](o) / [Zr(OH)_i^{4-i}](a)$ . K<sub>d</sub> Zr shows increasing continuously with increasing acidity of the aqueous phase. The Zr do not shows competition with nitric acid to form the coordination bonds with TBP. The increasing of K<sub>d</sub> Zr is caused by increasing of HNO<sub>3</sub> concentration [16]. K<sub>d</sub> Zr also increase with increasing concentration of TBP, hence by using of 30 % TBP-kerosene is an effort decrease the concentration of TBP to suppress K<sub>d</sub> Zr and then it can increase the separation factor of U/Zr namely SF<sub>(U/Zr)</sub> = K<sub>d</sub> U / K<sub>d</sub> Zr.

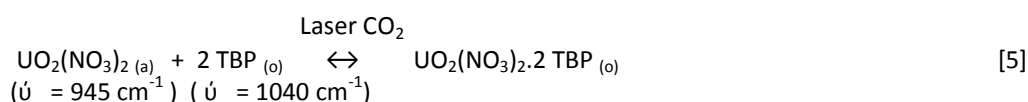
The increasing of separation factor for U from Zr and Ru has been carried out among others by chemical treatment that difficult (complicated) and expensive, however it has not obtained yet the satisfactory results. In this assessment, the application of laser radiation to be exposed on the extraction process of U using TBP-kerosene is one effort to increase the Kd U and SF<sub>(U/Zr)</sub> can be expected to give satisfactory results.

### 3.3. Development of Uranium Separation Process by Laser Radiation

Based on the generally schematic of the chemical separation by laser radiation excitation (Figure 1), it was carried-out the application research of laser radiation using CO<sub>2</sub> and N<sub>2</sub> laser pulses to increase Kd U on extraction for simulation liquid radioactive waste in HNO<sub>3</sub> solution as aqueous phase with organic phase of TBP in kerosene (system of HNO<sub>3</sub>-TBP/kerosene).

#### a. Application of CO<sub>2</sub> Laser

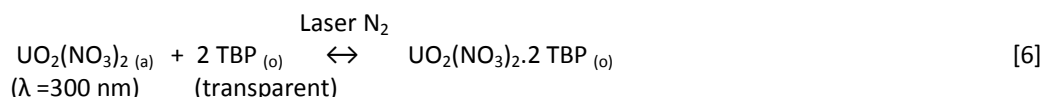
The CO<sub>2</sub> laser pulses emitted infrared radiation in wave number  $\nu = 944 \text{ cm}^{-1}$  can increase Kd U at 100 %. The extraction process according to the reaction equation as follows [17] :



At the equation [5], the species of uranyl nitrate compound UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> in aqueous phase absorb radiation energy of CO<sub>2</sub> laser at wave-number  $\nu = 945 \text{ cm}^{-1}$ , and then uranyl nitrate is excited to higher vibration energy level. Molecules of uranyl nitrate excited will be more reactive than the other molecules (having vibration energy level in ground state) to form the coordination bonds with TBP molecules, so that the uranyl nitrate more easy to be extracted into organic phase (TBP-kerosene), and it occur the increasing of Kd U. It was reported that the extraction of uranyl nitrate using TBP can be increased 100 % by application of the CO<sub>2</sub> laser pulses 3 MW at wave-number of absorption for uranyl ion (UO<sub>2</sub><sup>++</sup>)  $\nu = 945 \text{ cm}^{-1}$  [17].

#### b. Application of Nitrogen (N<sub>2</sub>) Laser

Application of nitrogen (N<sub>2</sub>) laser pulses emitted ultraviolet radiation at peak of wave-length  $\lambda = 337.1 \text{ nm}$  also can increase Kd U in the extraction process with the reaction equation as follows [19] :



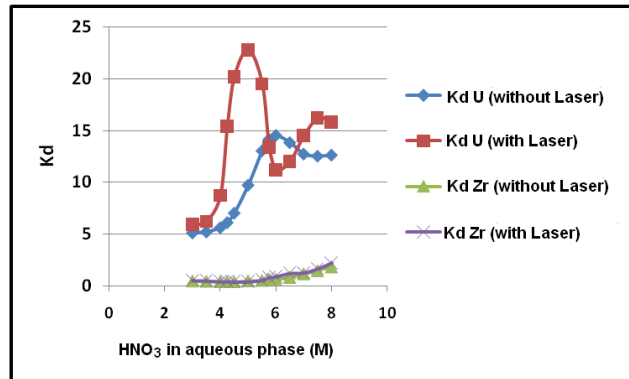
In the equation [6], the species of uranyl nitrate compound UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> in aqueous phase absorb radiation energy of N<sub>2</sub> laser at wave-length  $\lambda = 300 \text{ nm}$ , and then uranyl nitrate is excited to higher electronic energy level. Molecules of uranyl nitrate excited will be more reactive than the other molecules (having electronic energy level in ground state) to form the coordination bonds with TBP molecules, so that the uranyl nitrate more easy to be extracted into organic phase (TBP-kerosene), and it occur the increasing of Kd U.

Application of N<sub>2</sub> laser pulses to increase the separation of U and Zr have been studied using simulation liquid radioactive waste in HNO<sub>3</sub> solution as aqueous phase with 30 % TBP in kerosene as organic phase (system of HNO<sub>3</sub>- 30 % TBP/kerosene). Concentration of U and Zr contained in the simulation waste is 1000 mg/litre respectively, and molarity of HNO<sub>3</sub> 1-8 M. The effect of N<sub>2</sub> laser pulses on Kd U, Kd Zr and separation factor SF<sub>(U/Zr)</sub> are shown in Figure 2 and Figure 3 respectively.

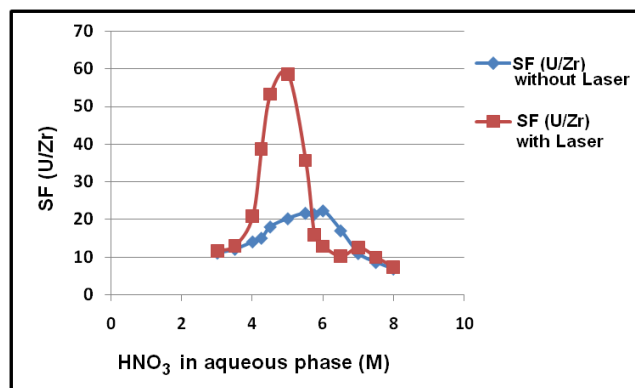
In Figure 2, the application of N<sub>2</sub> laser radiation pulses can increase Kd U and the optimum conditions can be obtained at concentration 5 M HNO<sub>3</sub>, whereas Kd Zr is very low and it not seen an increase in the presence of N<sub>2</sub> laser radiation pulses. Uranyl nitrate UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> and zirconium nitrate Zr(OH)<sub>i</sub>(NO<sub>3</sub>)<sub>4-i</sub> respectively absorb energy of of N<sub>2</sub> laser pulse radiation, but Kd U extremely higher than Kd Zr, in this case there are three factors that cause the Kd U and Kd Zr are quite different are as follows :

- a. Reactivity of uranyl nitrate is higher than zirconium nitrate to form the coordination bonds with TBP, so that the mass transfer of uranyl nitrate into organic phase (TBP-kerosene) more easily.

- b. Absorption coefficient of N<sub>2</sub> laser radiation energy for uranyl nitrate much higher than zirconium nitrate, thus increasing the reactivity of uranyl nitrate to form the complex compound with TBP is much higher than the zirconium nitrate.
- c. The value of K<sub>d</sub> depends on the concentration of TBP and HNO<sub>3</sub>, the increasing of the concentration of TBP can increase K<sub>d</sub> U is high enough in 5-6 M HNO<sub>3</sub>, whereas the increasing of K<sub>d</sub> Zr is relatively low and optimum in 8 M HNO<sub>3</sub>.



**Figure 2.** Effect of N<sub>2</sub> Laser pulse radiation on K<sub>d</sub> U and K<sub>d</sub> Zr in extraction system of HNO<sub>3</sub>-30%TBP/kerosene (irradiation of laser for 90 minutes at voltage 100 volt) [18].



**Figure 3.** Effect of N<sub>2</sub> Laser pulse radiation on SF<sub>(U/Zr)</sub> in extraction system of HNO<sub>3</sub>-30%TBP/Kerosene (irradiation of laser for 90 minutes at voltage 100 volts) [18].

Based on these three factors, the use of a low concentration of TBP (30 % TBP-kerosene), K<sub>d</sub> Zr can be suppressed and K<sub>d</sub> U can be increased in the presence N<sub>2</sub> laser pulse radiation, so the SF<sub>(U/Zr)</sub> can also be increased as shown in Figure 3. According to the mechanism of reaction (1) and (2), extraction of uranyl nitrate by TBP will increase with increasing the concentrations of HNO<sub>3</sub> and NO<sub>3</sub><sup>-</sup> ion, but in reaction equation (3) the higher the concentration of HNO<sub>3</sub>, the reaction shifts to the left again, so K<sub>d</sub> U decrease and it is obtained the optimum K<sub>d</sub> U at around 6 M HNO<sub>3</sub>.

Presence of N<sub>2</sub> laser pulse radiation, the optimum conditions of K<sub>d</sub> U shifted toward lower concentrations of HNO<sub>3</sub> namely in 5 M HNO<sub>3</sub>. This is caused the reactivity of uranyl nitrate and HNO<sub>3</sub> to form the complex compound with TBP greater in the presence of N<sub>2</sub> laser radiation, because HNO<sub>3</sub> also has absorption at  $\lambda = 300$  nm with the absorption coefficient smaller than the absorption coefficient of uranyl nitrate. Optimum point of K<sub>d</sub> U look sharper, indicating that complex formation of [HNO<sub>3</sub>.TBP] and [UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>.2TBP] are accelerated by the presence of N<sub>2</sub> laser radiation. K<sub>d</sub> U increase again on HNO<sub>3</sub> concentration higher than 6 M, this is because the reaction in equation (1) and (2) back reaction shifts to the right and increase the species of uranyl nitrate compound which can be extracted into the organic phase. In the optimum conditions (Figure 2), the use of N<sub>2</sub> laser can increase the K<sub>d</sub> U of 9.7 to 22.8 or increase of 135% which is relatively higher than the use of CO<sub>2</sub> laser which can only increase

the Kd of 100%, and N<sub>2</sub> laser (Figure 3) can increase the SF (U/Zr) from 20.2 to 58.5 or increase of 189% (or to 2.89 fold).

### 3.4. Adaptation of the Use of N<sub>2</sub> Laser pulses on Treatment of HLLW from RPI and RMI by Extraction Process with Systems of HNO<sub>3</sub> - 30% TBP / kerosene

In Indonesia, the HLLW generated from the production of radioisotope <sup>99</sup>Mo from irradiation of uranium enriched 93 wt% <sup>235</sup>U in Radioisotope Production Installations (RPI). The HLLW also generated from post-irradiation examinations of nuclear fuel (uranium enriched 20 wt% <sup>235</sup>U) in Radiometalurgi Installation (RMI). Both types of HLLW contains radionuclides of fission products, uranium, and TRU in small quantities. These wastes such as waste generated from the reprocessing of spent nuclear fuel. The data of HLLW and LWTRU from the <sup>99</sup>Mo radioisotope production in RPI and from post-irradiation examinations of nuclear fuel in RMI are shown in Table 6.

In Table 6 shows that the content of U in the HLLW-I was still very high which needs to be separated from the fission product elements. The treatment technology of HLLW generated from RPI has been developed through a process of solvent extraction using diethyl hexyl phosphoric acid to separate U and the fission product elements in the HLLW-I [19,20]. Whereas the treatment technology of HLLW generated from IRM has also been developed through the process of solvent extraction using TBP-dodecan to separate U from the fission product elements in the HLLW-I [21].

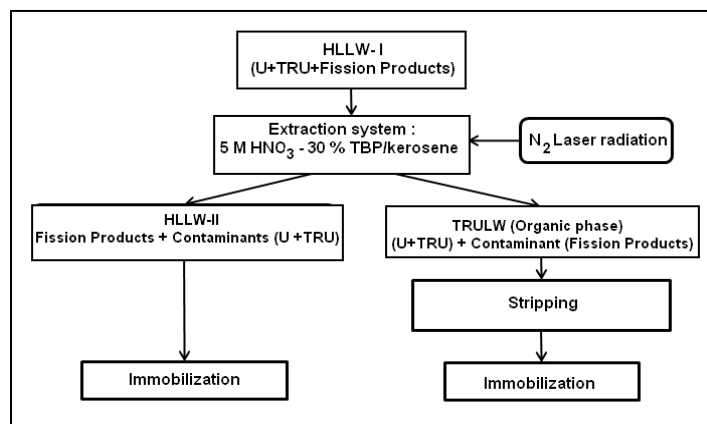
**Table 6.** Data of HLLW generated from the <sup>99</sup>Mo radioisotope production in RPI and from post-irradiation xaminations of nuclear fuel in RMI [19,20,21].

Waste	HLLW from RPI [ 19,20]	HLLW from RMI [21]
<ul style="list-style-type: none"> <li>Waste type and contents of radionuclides.</li> </ul>	HLLW-I : remaining uranium ~200 g U/litre, fission products (mayor nuclides are : <sup>99</sup> Nb, <sup>63</sup> Ni, <sup>55</sup> Fe, <sup>54</sup> Mn, <sup>58</sup> Co, <sup>59</sup> Fe, <sup>51</sup> Cr), TRU (Pu and minor actinides are : Np, Am, Cm), in nitric acid solution.	HLLW-I : reamaining uranium, fission products (mayor nuclides are : <sup>109</sup> Cd, <sup>144</sup> Ce, <sup>106</sup> Ru, <sup>134</sup> Cs, <sup>137</sup> Cs, <sup>60</sup> Co, <sup>57</sup> Co, <sup>131</sup> Ba, <sup>226</sup> Ra, <sup>154</sup> Eu, <sup>82</sup> Br), and TRU (Pu and minor actinides are : Np, Am, Cm), in nitric acid solution.
<ul style="list-style-type: none"> <li>Contents of uranium (U)</li> </ul>	Still very high, it is needed separation of fission products with U and actinides to produce HLLW-II and LWTRU.	Still very high, it is needed separation of fission products with U and actinides to produce HLLW-II and LWTRU.
<ul style="list-style-type: none"> <li>Quantity of waste per year</li> </ul>	120 litres(2 drums) per year with total of activity 600 Ci.	10 litres per year with total of gamma activity of 122,608 Bq/ml (= 3,3.10 <sup>-3</sup> Ci/m <sup>3</sup> ).

Adaptation of technology to increase the separation process of U and TRU elements with fission product elements can be done through the process of extraction with the solution system of 5 M HNO<sub>3</sub>-30% TBP/kerosene. The solvent used in the extraction process is same with the solvent used in advance extraction process so do not add the type of solvent. In accordance with the assessment discussed above, the increasing of Kd U and SF (U/Zr) has been successfully used N<sub>2</sub> laser and CO<sub>2</sub> laser pulse radiations. The use of N<sub>2</sub> laser pulse radiation is relatively better than the use of CO<sub>2</sub> laser pulse radiation. Adaptation of HLLW treatment process technology generated from RPI and IRM through the extraction process using N<sub>2</sub> laser pulse is shown in Figure 4.

In Figure 4, the development of HLLW treatment is performed by the extraction process for separation of U and TRU from fission product elements so that is obtained HLLW-II containing the fission product elements which is free from the contaminants of U and TRU, and the organic phase as LWTRU containing U and TRU which is free from contaminants of fission product elements. Further the HLLW-II is performed immobilization through solidification process using the matrix material of glass borosilicate or synroc. Whereas the LWTRU which is the long life alpha radioactive liquid waste is performed immobilization by solidification process using the matrix material of asphalt (bitumen), polymer, or synroc [22].





**Figure 4.** Adaptation of HLLW treatment process technology generated from RPI or RMI through the extraction process with solution system of 5 M HNO<sub>3</sub> -30% TBP / kerosene using N<sub>2</sub> laser pulse radiation.

#### 4. Conclusion

The N<sub>2</sub> laser radiation source that emits of ultraviolet radiation with maximum wavelength of 337.1 nm can increase the Kd U and SF<sub>(U/Zr)</sub> in the extraction with solution system of HNO<sub>3</sub>-30% TBP/kerosene and optimum at 5 M HNO<sub>3</sub>. The use of N<sub>2</sub> laser pulse radiation (for 90 minutes and voltage of N<sub>2</sub> laser source of 100 volts) can increase the Kd U from 9.7 (without N<sub>2</sub> laser irradiation) to become 22.8 or increase of 135% and the increasing of SF<sub>(U/Zr)</sub> from 20, 2 to become 58.5, or increase of 189%. The increasing through excitation of electronic energy levels of the uranyl nitrate compounds by absorption of the N<sub>2</sub> laser pulse radiation, resulting the uranyl nitrate compounds are more reactive with TBP to form the complex of [UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>.2TBP] that can be extracted into the organic phase of 30% TBP/kerosene. This fact shows the same as in the excitation of vibrational energy levels using the CO<sub>2</sub> laser that emits infrared radiation at maximum wave number  $\nu = 945 \text{ cm}^{-1}$ . The use of N<sub>2</sub> laser pulse radiation provides increasing of Kd U is relatively higher than the use of CO<sub>2</sub> laser pulse radiation which only gives increasing of Kd U by 100%. In Indonesia, assessment for adaptation of the separation technology by extraction for separation of U process using 30 % TBP-kerosene solvent should be carried-out as alternative for treatment the HLLW generated from <sup>99</sup>Mo radioisotope production in RPI and from post irradiation examination of nuclear fuel in RMI.

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