Evaluation of the Effects of Advanced Voloxidation Process on Pyroprocessing

I. Radiation and Decay Heat Analysis of the Advanced Voloxidation Process

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제 출 문

한국원자력연구원장 귀하

본 보고서를 사용후핵연료 고도 휘발성 산화공정 기술개발 과제에서 고도 휘발성산화공정이 파이로프로세싱에 미치는 영향평가 관련 수행한 “고도 휘발성 산화공정의 방사능 및 붕괴열 분석- Radiation and decay heat analysis of the Advanced Voloxidation process”의 기술보고서로 제출 합니다.

제 목 : Evaluation of the Effects of Advanced Voloxidation process on Pyroprocessing - I. Radiation and decay heat analysis of the Advanced Voloxidation process

2008 년 9 월

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KAERI has been developing a voloxidation process as a head-end process of pyroprocessing technology with INL (Idaho National Laboratory). It was named as the Advanced Voloxidation process by KAERI and INL. This Advanced Voloxidation process consists of more than two steps. The first step is an oxidative decladding step at ~500 °C. The second step is a volatilization step of gaseous nuclides at a vacuum and ~1200 °C conditions. If necessary, particle size control step and reduction step can be added to these steps.

The Advanced Voloxidation process has many potential merits over a standard voloxidation process, which has been carried out at ~500 °C. It can mostly remove the gaseous nuclides such as Kr, Xe, C-14, and H-3. It can also remove semi-volatile nuclides such as Cs, I, Te, Ru, Mo, Rh, etc. Among these nuclides, Cs is a highly radioactive and decay heat eminent nuclide. I-129 and Tc-99 and C-14, etc. are long-lived fission products. Considerable amount of such semi-volatile nuclides are also removed in the Advanced Voloxidation process. On the while, most of volatile and semi-volatile nuclides except tritium cannot be removed significantly in a standard voloxidation process.

This report describes how much a radioactivity level can be reduced by this Advanced Voloxidation process. It also presents the element and radioactivity distributions of the nuclides in fresh spent PWR fuels, those after the advanced voloxidation process, and those of the gaseous fission products released from the advanced voloxidation process.

Analysis was carried out for spent PWR fuels with a burn-up of 45,000 MWD/MTU and an initial enrichment of 4.5%. The calculated radioactivity reduction ratio of the spent PWR fuel meat by the Advanced Voloxidation process increases with the cooling time from 26% of discharge to 43~50% after 3 years cooling. The calculated decay heat reduction ratio increases with the cooling time from 39% of discharge up to 57% of 5 yrs cooling, and then decreases down to 40~50% after 10 yrs cooling. Cs is the most important element for off-gas treatment in view of radioactivity, decay heat, and mass aspects.
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1. INTRODUCTION

KAERI has been developing a voloxidation process as a head-end process of pyroprocessing technology with INL (Idaho National Laboratory)[1, 2]. It was named as the Advanced Voloxidation process by KAERI and INL[3]. This Advanced Voloxidation process consists of more than two steps[3, 4]. The first step is an oxidative decladding step at ~500 °C. The second step is a volatilization step of gaseous nuclides at a vacuum and ~1200 °C conditions. If necessary, particle size control step and reduction step can be added to these steps.

The Advanced Voloxidation process has many potential merits over a standard voloxidation process, which has been carried out at ~500 °C[5]. It can mostly remove the gaseous nuclides such as Kr, Xe, C-14, and H-3[6]. It can also remove semi-volatile nuclides such as Cs, I, Tc, Ru, Mo, Rh, etc[1]. Among these nuclides, Cs is a highly radioactive and decay heat eminent nuclide. I-129 and Tc-99 and C-14, etc. are long-lived fission products. Considerable amount of such semi-volatile nuclides are also removed in the Advanced Voloxidation process. On the while, most of volatile and semi-volatile nuclides except tritium cannot be removed significantly in a standard voloxidation process[5, 6]. Expected demerits of standard voloxidation process are presented in Fig. 1, and expected merits of the Advanced Voloxidation process in Fig. 2.

This report describes how much a radioactivity level can be reduced by this Advanced Voloxidation process. It also presents the element and radioactivity distributions of the nuclides in fresh spent PWR fuels, those after the advanced voloxidation process, and those of the gaseous fission products released from the advanced voloxidation process.

2. Calculation basis

Radioactivity analysis was carried out for spent PWR fuels with a burn-up of 45,000 MWD/MTU, a cooling time of 5 years and an initial enrichment of 4.5% on the basis of 100 kg UO2. These conditions are based on the reference spent fuel used for designing the integrated pyroprocess process (10 MTHM/yr) in Korea. It was calculated by using the OREGEN-ARP code.
3. Results and Discussions

3.1 Spent PWR fuel

Fig. 3 shows radioactivity analysis result of spent PWR fuel. Radioactivity decreases sharply with cooling time in the initial cooling period due to short half-life nuclides. And then it slowly decreases with cooling time. Fig. 4 shows decay heat analysis result of spent PWR fuel. Decay heat also decreases sharply with cooling time in the initial cooling period due to short half-life nuclides. And then it slowly decreases with cooling time.

Fig. 5 shows major radioactive elements of spent PWR fuel. The major radioactive nuclides in the spent fuels are a Cs group(Cs-134 and Cs-137), Ba-137m(a daughter nuclide of Cs-137), Sr-90, Y-90(a daughter nuclides of Sr-90), a Pu group(Pu-238, Pu239, Pu-240, Pu-241 and Pu-242), and the other group(Kr, Ru, Rh, Pm and Eu, etc).

Fig. 6 shows major abundant fission products of spent PWR fuel. Mo, Ru, Xe, Cs, Ba are major rich fission products having more than 2,000 g/MTHM. Sr, Tc, Pd, Sm are also rich fission products having more than 1,000 g/MTHM. Fig. 7 shows major heat generating elements of spent PWR fuel. Sr, Y, Rh, Cs, Ba, Pu, Cm are major heat generating elements having more than 100 watts/MTHM.

3.2 Advanced Voloxidation process

Removal rates of the fission products are assumed based on KAERI, INL experimental data[1-2]. These are shown in Table 1. Removal rate of Cs is 98%. Those of Kr, Xe, H-3, C-14, I-129 are 100%. And, those of Tc, Ru, Rh, Te, Mo and Rb are 92%, 98%, 83%, 53%, 62% and 96%, respectively.

Considering the release rates of the fission products, the radioactivity reduction ratio of a spent PWR fuel meat after the advanced voloxidation process was calculated. To calculate the radioactivity, two secular equilibriums were considered. One is between Cs-137 and Ba-137m and the other is between Ru-106 and Rh-106. The half lives of Cs-137 and Ba-137m are 30 yrs and 2.6 min. Those of Ru-106 and Rh-106 are 368 days and 30 sec, respectively. This indicates that if Cs-137 and Ru-106 were removed, activities and decay heats of Ba-137 and Rh-106 could be considered to be disappearing in voloxidized fuel meat due to their short half-lives.
Fig. 8 shows activity reduction ratio by the Advanced Voloxidation process. The radioactivity reduction ratio increases with the cooling time from 26% of discharge to 43~50% after 3 years cooling. The radioactivity reduction ratio of a spent PWR fuel meat was 43% in the case of a 5 yr cooling. If the Advanced Voloxidation process is applied to pyroprocessing technology, it seems that long-term storage of spent PWR fuel is more desirable than short-term storage in view of radioactivity reduction ratio. Radioactivity reduction is mainly due to removal of Cs. On the other hand, the radioactivity reduction ratio of DUPIC process is almost the same as that of Advanced Voloxidation process[7]. The release of Cs during the DUPIC process occurs in the sintering process of DUPIC pellets.

Fig. 9 shows decay heat reduction ratio by the Advanced Voloxidation process. The decay heat reduction ratio increases with the cooling time from 39% of discharge up to 57% of 5 yrs cooling, and then decreases down to 40~50% after 10 yrs cooling. Only in view of decay heat removal ratio, 5 yrs cooling spent fuel seems to be good for advanced voloxidation process. However, it is considerate to determine optimum cooling time of spent fuel. Various factors including radiation and decay heat levels, radiation removal ratio, and decay heat removal ratios, etc should be considered.

### 3.3 Voloxidized material

Fig. 10 shows radioactivity of the voloxidized material with cooling time. Radioactivity of the voloxidized material decreases with cooling time. Radioactivity of 5yr cooling material is 22,800 Ci/batch and that of 20 yrs cooling material is 11,100 Ci/batch, which is 48.7% of that of 5 yrs cooling one. Fig. 11 shows Decay heat of the voloxidized material with cooling time. Decay heat of the voloxidized material decreases with cooling time. Decay heat of 5yrs cooling material is 59.2 watts/batch and that of 20 yrs cooling material is 31.3 watts/batch, which is 52.9% of that of 5 yrs cooling one.

Major radioactive elements of the voloxidized material are shown in Fig. 12. The major radioactive elements are Sr, Y, Pm, Pu. Sr, Y is expected to be removed in the electroreduction step. Fig. 13 shows major rich elements of the voloxidized material. The major rich elements are Sr, Y, Mo, Pd, Ba, Sm, Np, Pu, Am. And, Fig. 14 shows major decay heat generating elements of the voloxidized material. The major heat generating elements are a Sr, Y, Eu, Pu, Am, Cm, etc.
3.4 Off-gas stream

Fig. 15 shows radioactivity of off-gas with cooling time. As can be seen, radioactivity of off-gases decreases with cooling time. Off-gas radioactivity from treatment of 5yrs cooling fuel is 19,300 Ci/batch and that of 20 yrs cooling fuel is 8,380 Ci/batch, which is 43% of that of 5 years one. And, Fig. 16 shows decay heat of off-gas with cooling time. Decay heat of off-gas decreases with cooling time. Off-gas decay heat from treatment of 5yrs cooling fuel is 59.6 watts/batch and that of 20 yrs cooling fuel is 9.2 watts/batch, which is 15% of that of 5 years one.

Major radioactive elements of off-gas stream are shown in Fig. 17. Cs is the highest radioactive nuclide in the off-gas stream. Its portion is 86 %. Kr and Ru are also highly radioactive nuclides. Fig. 18 shows major rich elements of off-gas stream. Ru, Cs, Xe, and Mo are highly abundant elements having over 100g/batch in the off-gas stream from the Advanced Voloxidation process. (Xe 36%, Cs 19%, Ru 15%, Mo 14%). Kr, Rh, Te, I, Tc, and Rb are also abundant elements. Major decay heat generating elements of off-gas stream are shown in Fig. 19. Cs is the most highly decay heat generating element. The decay heat of cesium is 46 watts/batch and its portion is 97 %. In this regard, the off-gas trapping system shown in Fig. 20 has been developed by KAERI and INL for completing the technology of the Advanced Voloxidation process [3].

The roll of the Advanced Voloxidation is considered to be very important for pyroprocessing in view of radioactivity reduction, decay heat reduction, easiness of Cs treatment, I-129 treatment, Tc-99 treatment, increase of treating capacity of electroreduction process, etc[8].
4. CONCLUSIONS

KAERI has been developing an advanced voloxidation process as a head-end process of pyroprocessing technology with INL(Idaho National Laboratory). In this study, the radioactivity reduction level and decay heat reduction level by the Advanced Voloxidation process were investigated. Analysis was carried out for spent PWR fuels with a burn-up of 45,000 MWD/MTU and an initial enrichment of 4.5%.

The calculated radioactivity reduction ratio of the spent PWR fuel meat by the Advanced Voloxidation process increases with the cooling time from 26% of discharge to 43~50% after 3 years cooling. The calculated decay heat reduction ratio increases with the cooling time from 39% of discharge up to 57% of 5 yrs cooling, and then decreases down to 40~50% after 10 yrs cooling. Cs is the most important element for off-gas treatment in view of radioactivity, decay heat, and mass aspects.
REFERENCES


Table 1. Removal percent (%) of fission products by the Advanced Voloxidation process.

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<th>H-3</th>
<th>C-14</th>
<th>Kr-85</th>
<th>I-129</th>
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<td>100</td>
<td>100</td>
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<td>98</td>
<td>92.3</td>
<td>97.6</td>
<td>82.7</td>
<td>53.3</td>
<td>61.7</td>
<td>96</td>
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Fig. 1. Expected demerits of standard voloxidation process.

- Removes Kr, I, C-14 just by ~30%
- Difficult to treat iodine from molten salt of electroreduction process
- Makes highly heat generating Cs be added into ceramic waste
- Generates highly heat generating HL ceramic waste → limits the disposal amount per unit area
- Packing density : ~2.0
- Limitation of treatment capacity
- Not easy to treat noble metals, such as Ru, Tc, Mo, Rh, etc.
Fig. 2. Expected merits of the Advanced Voloxidation Process.

- Removes most of Kr, I, C-14, Cs, Tc, Ru, etc
- Reduces radiation effect on downstream processes due to the preremoval of highly radioactive cesium (reduction of shielding thickness, increase of material life time)
- Expected packing density : > 3, so treatment capacity can be increased by >50%
- Reduces heat generation of ceramic waste due to the preremoval of cesium – increase of disposal amount per unit area
- Reduces the treatment burden of noble metals, such as Ru, Tc, Mo, Rh, etc

Spent Fuel → Advanced Voloxidation (1,200 °C, Vacuum) → Ar → Electrolytic Reduction In Molten Salt → Li₂O + LiCl → Metal Ingot → Electorefiner → TRU Metal Fuel → High Level Waste → Permanent Disposal → Recycle to SFR
Fig. 3. Radioactivity of spent PWR fuel with cooling time.
Fig. 4. Decay heat of spent PWR fuel with cooling time.
Fig. 5. Major radioactive elements of the spent PWR fuel.
Fig. 6. Major abundant fission products of the spent PWR fuel.
Fig. 7. Major heat generating elements of the spent PWR fuel.
Fig. 8. Activity reduction ratio by the Advanced Voloxidation Process.
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Fig. 10. Radioactivity of the voloxidized material with cooling time.
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Fig. 15. Radioactivity of off-gas with cooling time.
Fig. 16. Decay heat of off-gas with cooling time.
Fig. 17. Major radioactive elements of off-gas stream.
Fig. 18. Major rich elements of off-gas stream.
Fig. 19. Major decay heat generating elements of off-gas stream.
* Trapping methods and conditions might change with further experiments.

Fig. 20. Schematic diagram of off-gas treatment system for the Advanced Voloxidizer.
**BIBLIOGRAPHIC INFORMATION SHEET**

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**Abstract (15-20 Lines)**
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**Subject Keywords**
Advanced Voloxidation, Radioactivity, Decay Heat, Reduction ratio, ORIGEN-ARP, Off Gas, Spent fuel, Fission gases, Cesium
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| 제목 / 부서 | 고도 휘발성산화공정이 파이로프로세싱에 미치는 영향평가/ I. 고도 휘발성 산화공정의 방사능 및 붕괴열 분석 |
| 주저자 및 부서명 | 박 장진 (재순환핵연료기술개발부) |
| 공동저자 및 부서명 | 박 창제, 전종익, 이 재원, 신 전명, 박 근일, 송 기찬 (재순환핵연료기술개발부) |

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| 참고사항 |
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| 연구위탁기관 | 계약 번호 |
| 초록 (15-20 줄내외) |

KAERI 는 INL 과 파이로프로세싱의 전처리 공정으로서 휘발성산화공정을 개발하고 있으며 이를 고도 휘발성산화공정으로 명명하였다. 이 보고서는 고도 휘발성산화공정 중 방사능과 붕괴열이 얼마나 감소하였는지 기술하고 있다. 또한, 사용후핵연료, 고도 휘발성산화 후 물질, 배기가스 중에서 각 element 들의 무게, 방사능, 붕괴열을 분석하였다. 분석은 연소도 45,000 MWD/MTU, 초기농축도 4.5%인 PWR 사용후핵연료에 대하여 분석하였다. 고도 휘발성산화에 의해 저감된 방사능 비율은 방출시 26%에서 3 년이 지나면 43% ~ 50%까지 증가하였다. 붕괴열은 방출시 39%에서 5 년 냉각 핵연료는 57%로 더 냉각하면 40~50%로 감소하였다. 여러 핵종 중 세슘은 방사능, 붕괴열, 무게 측면에서 배기제처리에 있어 가장 중요하다고 판단된다.

| 주제명키워드 | 고도 휘발성 산화공정, 방사능, 붕괴열, 감소비율, ORIGEN-ARP, 배기체, 사용후핵연료, 핵분열기체, 세슘 |
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