TECHNOLOGY OPTIONS FOR FUTURE RECYCLING

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ABSTRACT

Recycling of nuclear material is indispensable, not only for using valuable resources but also for reducing the debt which we may leave to the next generations. Advanced reprocessing technologies have been developed in several countries to deal with the diversification of nuclear fuels. Also technologies derived from reprocessing or other fuel cycle areas have continued to be developed in terms of recycling. Cost effectiveness and waste-free processing are increasingly important factors in the applicable of an alternate recycling policy. This paper introduces an example of the studies in this field conducted in some countries including Japan and considers the establishment of effective recycling methodologies taking into account the uncertainty of future recycling policy.

INTRODUCTION

At present, nuclear energy is one of the major energy resources and some countries will continue to rely heavily on nuclear energy at least for several decades in order to meet the growing energy demand and to maintain and improve the current standard of living.

Nuclear energy, along with other potential energy sources, will be the basis for the future energy-mix system. Effective utilization of nuclear energy, which is economically established technology, is an obligation of our generation.

Future development of advanced reactor technologies and surrounding fuel cycle technologies should take into account the following factors:

- Safety of operation
- Reduction of environment impact (radioactive waste, CO_2 emission)
- Cost competitiveness (near-term and long-term)
- Nuclear proliferation resistance and international safeguards regime of nuclear material
- Effective use of energy potential of uranium (^{238}U) by fast neutron system
- Assurance of stable acquisition of energy resources
- World wide infrastructure of the fuel cycle

Since these factors sometimes conflict with each other, it is anticipated that it will be difficult to find the best optimization. This paper addresses topics which have advantages to satisfy many of the factors mentioned above.

a) The application of a crystallization technique to reprocessing has the potential to contribute for:

- Reduction of process waste
- Cost effectiveness from simplified process design
- Plant operation safety
- Nuclear proliferation resistance

b) Effective recycling options for uranium recovered from reprocessing and depleted uranium from enrichment also have the potential to contribute for:

- Effective use of uranium reserves
- Minimized risk arising from storage of uranium
- Reduction of the debt for the future.

REPROCESSING USING CRYSTALLIZATION TECHNOLOGY

History

Selective crystallization is widely applied for commercial chemical purification technology. Selective separation can be achieved by using concentration differences or solubility differences of the compounds in aqueous solution. Normally the required compound is separated as crystals by cooling the solution, while other compounds remain in the solution.

The application of crystallization techniques to the spent nuclear fuel reprocessing was first reported in 1980s (Henrich, 1987). Originally this technique was intended to be applied to the uranium purification or the plutonium purification process after the solvent extraction.

FIGURE 1 shows the crystallization temperature of uranium nitrate hydrate (UNH) – nitric acid solutions in water (Hart, 1958). Removal of impurities, such as fission products or other actinide elements, is possible by cooling saturated UNH solution and recovering UNH as crystals. Impurities remain in the solution because a concentration of UNH is much higher than those of impurities.

Plutonium nitrate hydrate (PuNH) has similar crystallization property as UNH. Purification of PuNH can be attained in same way.

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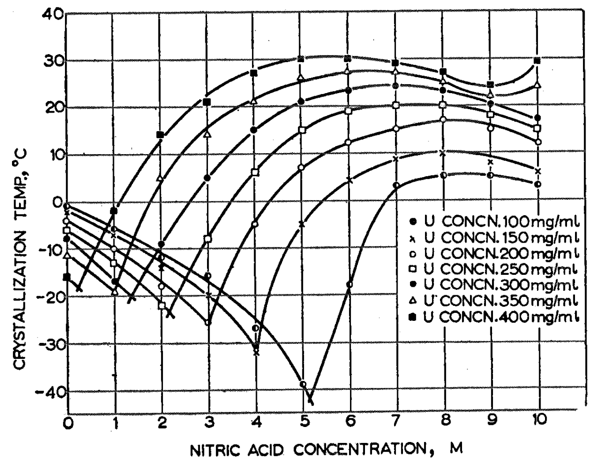

FIGURE 1. Crystallization temperature of UNH – Nitric acid solutions

Since the crystallization technique requires no organic solvents for extraction, the volume of liquid waste is expected to be significantly lower than the solvent extraction process. A large amount of organic waste is generated in the solvent extraction process due to degradation of organic solvent from radiation.

The size of equipment can be also reduced resulting in a reduction of facility size.

The results of bench-scale tests, conducted in various countries including Japan indicated advantages listed below.

- Relatively high decontamination factors which allow further processing of recovered uranium or plutonium for fuel fabrication purpose
- Adequate physical characteristics (suitable grain size for sedimentation and filtration)

Thus the crystallization technique is applicable to the recovery of moderately pure UNH or PuNH in a reprocessing facility.

Recently research has further expanded for the use of this technology in the area of the recovery of uranium directly from a solution of dissolved nuclear fuel.

Applicability

Crystallization can be applied to the following areas.

Application A (FIGURE 2) :

- After initial solvent extraction process of spent fuel solution, refine uranium and plutonium by the crystallization process respectively.
- Remove crystals of UNH and PuNH by filtration respectively.
- Return residual solution of crystallization to the initial solvent extraction stage, after concentration of residual solution if necessary.

Application B (FIGURE 3) :

- Recover uranium by the crystallization process from a solution of dissolved nuclear fuel (more than 80% of uranium will be separated as UNH crystals).
- Remove crystals of UNH by filtration. Send the UNH crystals to the uranium purification stage, if further purification is necessary.
- Remove impurities from residual solution after crystallization by the solvent extraction process.
- Separate uranium and plutonium by the solvent extraction process.
- Refine uranium and plutonium by crystallization.
- Remove crystals of UNH or PuNH by filtration.
- Return residual solution of crystallization to the solvent extraction stage for U/Pu separation, after concentration of residual solution if necessary.

Application C (FIGURE 4) :

- Recover uranium by crystallization from a solution of dissolved nuclear fuel. Adjust the U/Pu ratio in the residual solution after crystallization to the U/Pu ratio specified for the product by controlling the recovery rate of uranium.
- Remove crystals of UNH by filtration (Crystals can be used for FBR blanket fuel).
- Remove impurities from residual solution after crystallization by the solvent extraction process for direct preparation of MOX fuel.

A small amount of uranium and plutonium remains after the crystallization process, thus recycling of residual solution for further recovery is required.

Because the crystallization technique requires no organic solvent for extraction it has a great advantage for reprocessing spent fuels with higher radioactivity than normal LWR spent fuel, such as high burn-up fuel from light water reactor, MOX fuel and FBR fuel. The high radioactivity from such fuels causes significant damage to the organic solvent. A small scale solvent extraction process is added in the above cases to remove impurities or to separate uranium and plutonium. However the separation work by the solvent extraction is much less than conventional Purex process since a greater part of separation can be replaced by the crystallization process, especially in applications B and C.

Thus the crystallization has a merit that it can be applied to the advanced fuel recycling in the future.

Application C is unique in that it produces MOX fuel or FBR fuel directly with a much simplified process. Since high decontamination at the reprocessing facility is not necessary in the case of utilization of uranium and plutonium for FBR fuel, a 'low-decontamination purification' can also applied both for solvent extraction and crystallization in the application that it produces

- uranium which can be used as a blanket fuel of FBR
- mixture of uranium and plutonium with appropriate U/Pu ratio for MOX or FBR fuel fabrication.

The experimental results show that the Decontamination Factor (DF) at crystallization increases by repeating a washing procedure of the obtained crystals

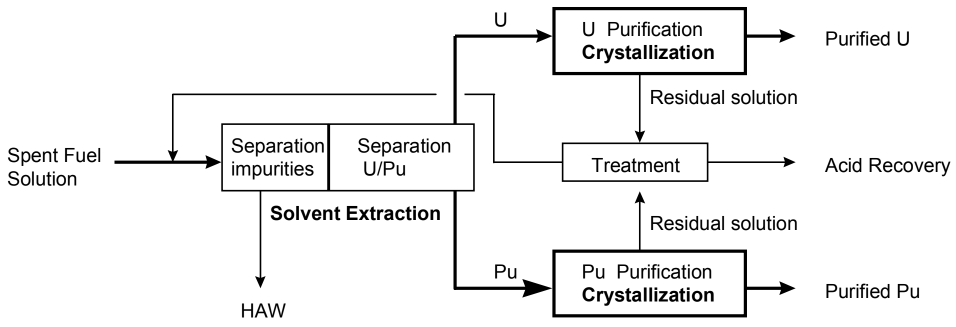

FIGURE 2. A Block Flow of Crystallization Process (Application A)

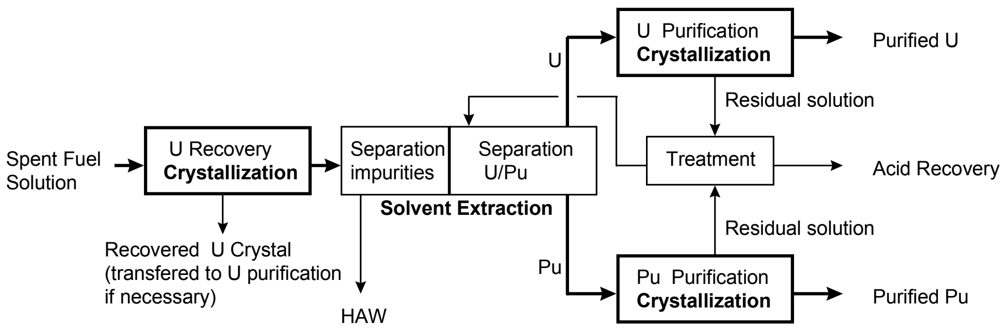

FIGURE 3. A Block Flow of Crystallization Process (Application B)

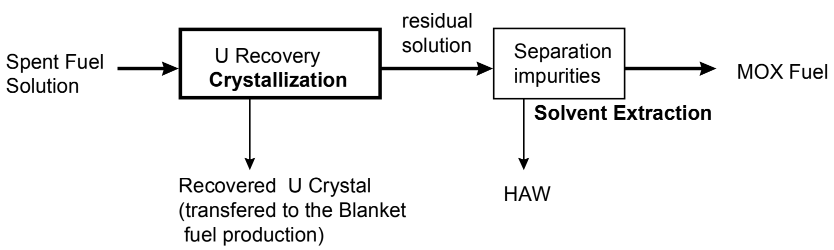

FIGURE 4. A Block Flow of Crystallization Process (Application C)

(Kurashima, 1994). Low DF type reprocessing can be attained by adjusting the number of washing procedures. Application C has a further advantage for nuclear proliferation prevention. Plutonium is extracted with uranium and other residual radio activities.

For safety of operation, since the crystallization technology does not require organic solvent, the risk of fire/explosion will be decreased. Operational conditions, such as pressure, temperature, are considered to be safe or same safety level comparing to the solvent extraction process.

For continuous operation, a kiln type apparatus, equipped with a screw conveying device has been proposed. Criticality safety was included in the design of the system (Kusaba, 1993). FIGURE 5 shows this type of apparatus.

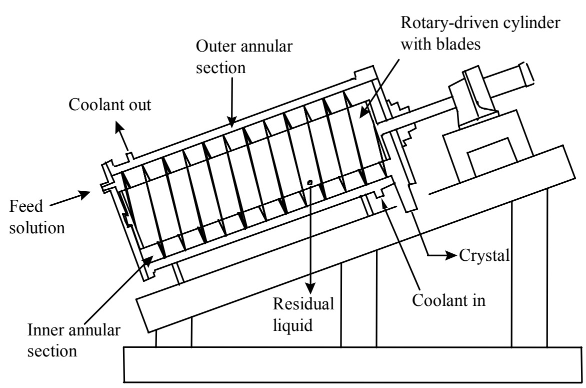

FIGURE 5. Apparatus for continuous operation

A rotary-driven cylinder is provided inside an inner section of the inclined apparatus. Feed solution is introduced from a lower inclined part of the apparatus into the annular section around the rotary-driven cylinder. Coolant circulates in the outer annular section. The feed solution cools gradually as it flows towards the outlet. Crystallized slurry in the inner annular section is removed by guide blades attached to the peripheral surface of the rotary-driven cylinder. Residual liquid is withdrawn from an upper inclined section of the apparatus.

Necessary steps for the utilization

Further R&D work is necessary in order to develop practical applications of this process as listed below. Some research has already been started in Japan (Okuno, 1999).

- For the detailed process design, experimental data using actual reprocessing solution containing plutonium or other radioactive impurities will be necessary. The process reliability and the process operability of the crystallization technology must be assured with several scale-up steps. Reliability of the process before and after the crystallization is also important because some changes in process condition or process design are expected compared to the Purex process.
- Issues relating to criticality, shielding, fire/explosion, and confinement must be examined and fully assured in the development of the apparatus. An evaluation of the safeguards approach and concern for proliferation must also be assured.
- Further quantitative evaluation of waste generated and reagents needed for operation is necessary to assess the environmental impact compared to the conventional Purex process or other technologies such as dry reprocessing process.
- Further cost evaluation of the crystallization technique is necessary to assess the process economy taking into account the cost of the necessary process development.

RECYCLING OF URANIUM

Uranium recovered from reprocessing

Uranium is separated from plutonium and other radioactive impurities during reprocessing. This uranium is not normally suitable for LWR fuel fabrication without re-enrichment. Occasionally, a small amount of such uranium can be used for FBR fuel. The effective utilization of the recovered uranium is discussed.

As to the conversion technique for UO_3 to UF_6 for the utilization as nuclear fuel via re-enrichment, there are some established methods, which are being used or ready for use. In Japan, a pilot plant test has been carried out. The process consists of UO_3 hydration stage to improve reactivity of the UO_3 powder, dehydration and reduction stage to UO_2, hydro-fluorination stage to UF_4, fluorination stage to UF_6 (Ohara, 1996). Effective conversion can be done at the hydro-fluorination stage by a combination of two fluidized beds and at the fluorination stage by a combination of flame reactor and fluidized bed.

The utilization of recovered uranium depends upon the contents of ^{232}U and ^{235}U. Both have a dependency on burn-up history (according to burn-up of fuel, ^{235}U decreases and ^{232}U increases).

- The ^{232}U daughter nuclides, ^{208}Tl, ^{212}Bi that emit high energy gamma rays, can be removed at the fluorination stage in a conversion process. However because ^{232}U can not be eliminated, these daughters will continue to build up. This limits re-use of high burn-up fuel.
- For ^{235}U content, the limit for re-use of the recovered uranium via re-enrichment is considered to be slightly higher than natural content under some assumption (Lannegrace, 1996).

Recovered uranium can be utilized according to the characteristics of the burn-up history as listed below. These options can compromise the factors like economics, safety or environmental impact.

a) If the irradiated fuel is low burn-up, recycling via an enrichment plant and a fuel fabrication plant, which are designed for natural-origin uranium, can be done with high purification by a combination of crystallization and solvent extraction. By this simple recycling method it is expected to increase the economic value of the reprocessed uranium.
b) In the case of high burn-up (low ^{235}U, high ^{232}U), storage of recovered uranium may be considered a better strategy. The crystallization technique is applicable both for high and low decontamination reprocessing. In the case of the storage of high burn-up recovered uranium, considering radiological safety, environmental impact, appropriate decontamination level can be adjusted depending on the energy policy and economics.
c) In the case of high burn-up, the utilization of CANDU type reactor to increase the burn-up of spent fuel from a light water reactor, known as DUPIC (Direct Use of Spent PWR Fuel In CANDUs) concept, may also be solution.

Depleted uranium

There are certain concern about depleted uranium resulting from enrichment facilities. Depending on the operation of the enrichment facility, a large amount of depleted uranium is produced and, in some cases, stored in the form of uranium hexafluoride (UF_6). This volatile chemical is not suitable for long term storage.

Although use of this material as blanket fuel in a breeder reactor would be an effective use of the energy potential of ^{238}U, utilization for this purpose has been delayed. In addition the current status of other options, listed below, which have been conducted in some countries, is limited and far from a large utilization of depleted uranium.

- Use in LWR as a MOX fuel after blending with plutonium
- Use in CANDU reactor
- Use in LWR after re-enrichment
- Use in LWR after mixing with HEU

Some utilization of uranium outside of the nuclear fuel cycle, including indirect use in nuclear fuel cycle, has been conducted taking into account several inherent heavy metal characteristics of uranium.

- Counterweight for inertia and balancing
- Catalyst
- Coloring for Ceramics
- Non-nuclear military applications such as ammunition, armored shielding
- Shielding material against gamma ray or neutron (e.g. container for transportation or storage of nuclear material)

In terms of the indirect use of depleted uranium, the utilization of the radiation protection characteristics of uranium metal in shielded containers is regarded as promising. Some of the container have been developed. Other characteristics of uranium metal, such as heat removal, stability against fission heat release, physical strength during transportation or storage, corrosion resistance, etc. are also suited for use in shielded containers. A feasibility study or development to improve the effectiveness of containers is continuing.

Relevant technologies listed below, which have been developed in Japan, can economically contribute to the utilization of depleted uranium for container material.

a) Conversion processes of UF_6 to U_3O_8

Conversion by fluidized bed process, in supplement with fluorine recovery process by distillation, has many advantages such as, waste free process, high density and high flowability of the product U_3O_8 powder, high recovery of fluorine etc. (Nishida, 1997).

b) Molten salt electrolysis of uranium oxide to uranium metal

Conversion by molten salt electrolysis was originally developed for the production of uranium metal for AVLIS. This electrolysis also has advantages for a waste free process, while another conventional method of UF_4 chemical reduction by magnesium produces MgF_2 waste (Takasawa, 1999).

CONSIDERATIONS FOR IMPROVING FUTURE RECYCLING

As described, there are many factors which must be taken into account for improving future recycling. The technologies addressed in this paper, which have the potential to contribute not only for the effective applications but also for the flexible applications, are considered to be very important to realize safety of operation, reduction of environmental impact, cost competitiveness and nuclear proliferation prevention.

The following direction can be considered as one of the approach for improving future recycling.

a) Crystallization technology

The crystallization technology should be further developed for the application to the advanced fuel cycle. This type of application, such as application C, introduced in this paper (direct recovery of uranium from a solution of dissolved nuclear fuel and direct preparation of MOX fuel), contributes not only to reduction of process wastes and safety of operation, but also to

- Cost reduction from more simplified process design than other types of applications
- Nuclear proliferation resistance

In addition, the advantage, that the crystallization process can fix U/Pu ratio in the residual solution after crystallization by controlling uranium recovery rate through changing a cooling condition, enables

- Steady operation of supplementary solvent extraction process without any operational condition changes.
- Reprocessing of wide variety of spent fuels at a same plant.

b) Technologies relating to the uranium recycling

Uranium recovered from the reprocessing plant should be used according to its characteristics (e.g. burn-up history). Depleted uranium also should be used in the fuel cycle to the extent possible.

All the conversion processes both for recovered uranium and depleted uranium, addressed in this paper, have advantages for

- Reduction of process waste
- Safety of operation

Depending upon the infrastructure associated with the fuel cycle, interim storage or final storage of spent fuel may, in some cases, be necessary. In this regard,

- Use of depleted uranium for the spent fuel storage containers

can be a solution for the utilization of depleted uranium. And considering very large quantities of depleted uranium and uncertainty of the future situation,

- Strategic stock pile as oxide ready for utilization

can be another solution.

FIGURE 6 shows an option for depleted uranium recycling. This option consists of several technologies introduced in this paper and enables

- Reduction of depleted uranium by the utilization for the containers
- Minimized risk arising from storage by storing the material as a stable chemical form
- Reduction of storing cost by storing the material with high bulk density
- Easy handling with high flowability in the case of re-use of the material

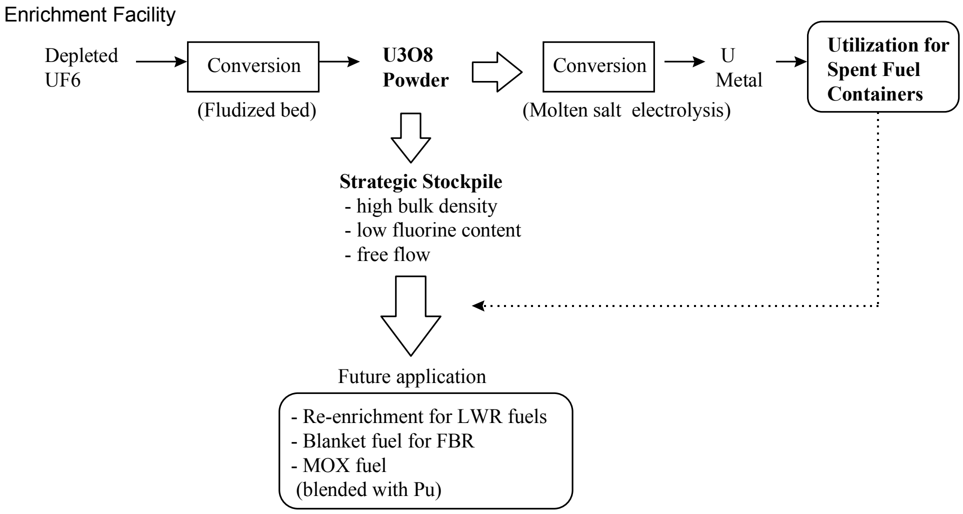

FIGURE 6. Option for Depleted uranium recycling

CONCLUSIONS

The Crystallization process has many advantages over presently used reprocessing technologies and is considered to be a promising candidate for the establishment of innovative nuclear fuel cycles. Some technologies relating to the effective use of uranium, introduced in this paper, has the potential to contribute to the future recycling options. With other useful developments, by the proper combination of the technologies, the future strategy for the effective use of resources can be established in timely manner.

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