Volume reduction of spent uranium catalyst used for production of acrylonitrile

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Background

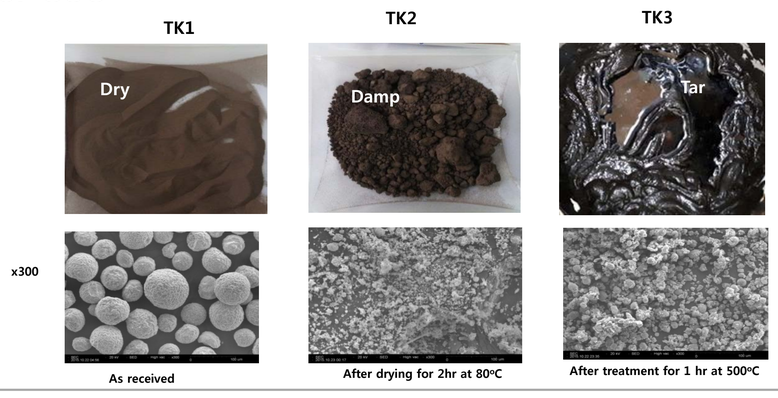
Generation of spent U-catalyst (SUC) used for production of acrylonitrile in Korea

- Approximately 7,100 drums of SUC have been stored on the generation site, which are supposed to be disposed to a low and intermediate level radioactive waste disposal site, starting in 2019.
- Disposal cost is very high (~ 12,500 US$/drum)
- Current state of the U-waste does not meet acceptance requirement of the disposal site because it contains powders and mixed with burnable materials (*e.g.* tar)
- Direct disposal of the wastes weakens original availability of the site for rad waste from NPP

Volume reduction of SUC to be disposed and treatment for acceptance requirement for the site are essential

Composition and status of spend U-catalyst

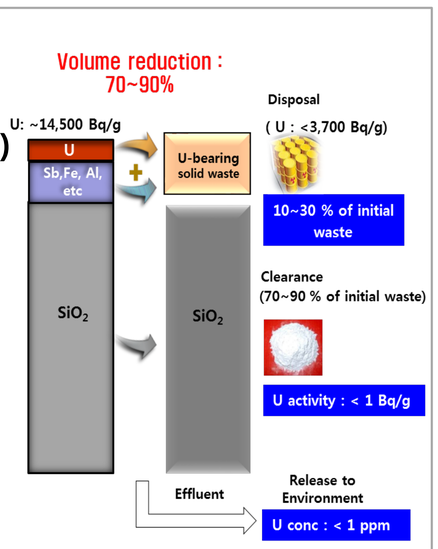
- **U,Sb,Fe,Al,V,Mo-mixed oxide/SiO_2**
  - SiO_2 : 50~60wt %, U (U-235 : ~0.2%) : 4~9 wt%, Sb : 15~25wt %, Fe : ~5 wt%,
  - Activity : 590 ~ 1,400 Bq/g (Activity of U component : ~14,500 Bq/g)
    (Maximum activity of α-emitting waste for the site in Korea : < 3,700 Bq/g)
- **3 types of SUC**



Concept of volume reduction of SUC

Principle

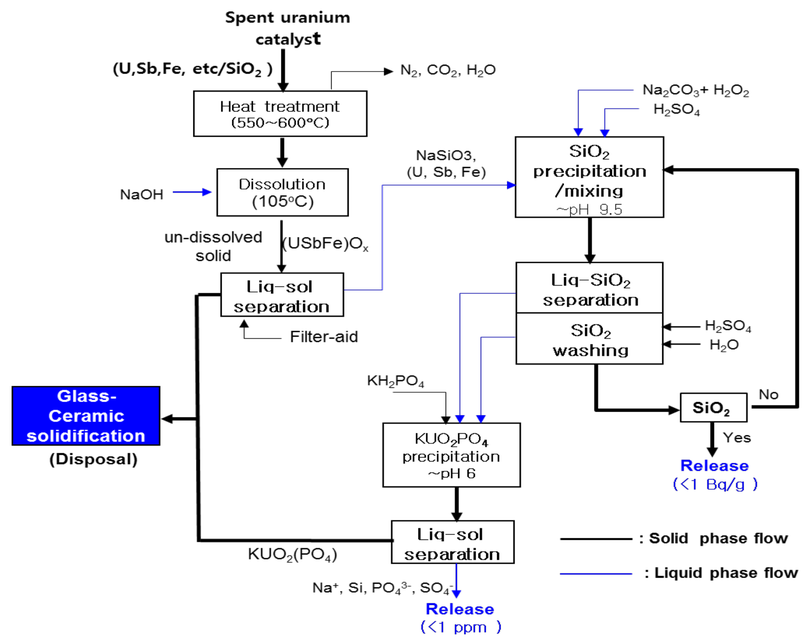
- **Volume reduction of SUC as much as possible**
- **Meeting acceptance criteria of U waste (<3,700 Bq/g)**
  - Selective removal of SiO_2, support of catalyst and its release to environment as clearance (<1 Bq/g)
  - Disposal of all other components together including U as a sable waste form



Criteria for process

- Simple operation
- Minimal 2nd waster generation
- Low cost
- High reliability

Process devised for volume reduction of SUC



(Bench scale test)

(Pilot scale test)

Evaluation of the process in bench and pilot scale based on lab scale test

Results of evaluation of process

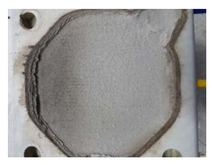
Selective dissolution of SiO_2 of SUC in alkaline solution

- SiO_2+2NaOH = Na_2SiO_3(Water glass) + H_2O (Si :30,000ppm)
- U co-dissolved : ~200 ppm ($UO_2(OH)_x^{y-}$)

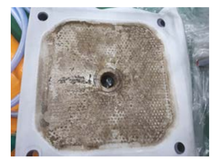
Volume reduction yield by dissolution

	Lab scale	Bench scale	Pilot scale
Volume Reduction (%)	69.7	75.7	76

Lab scale



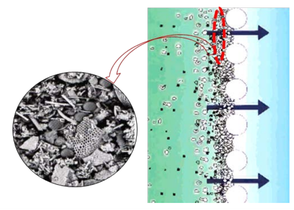
Bench scale



Pilot scale

Separation of undissolved material

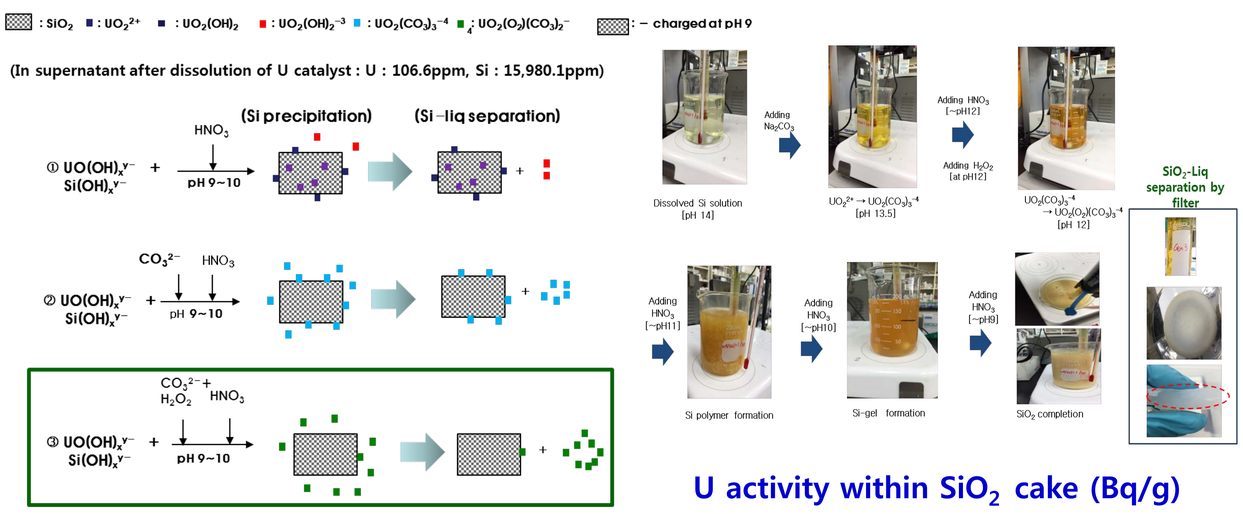
- Using filter press using filter aid (Diatomite)



Solid-liquid mechanism by filter aid

SiO_2 recovery and its purification

- Na_2SiO_3 + $2H^+$ = **SiO_2** (for clearance) + $2Na^+$ + OH^- (pH 9~10)
- To prevent entrainment of U into SiO_2 precipitation, dissolved U specie was changed to $UO_2(O_2)(CO_3)_2^{4-}$ species with high solubility.
- SiO_2 cake formed within filter press was washed by passing waster and acid through it.



U activity within SiO_2 cake (Bq/g)

	Bench scale	Pilot scale
Washing	3.6	0.355
1st purification	0.53	0.126
2nd Purification	0.44	<0.001

(which is acceptable to release limit)

Bench scale

Pilot scale

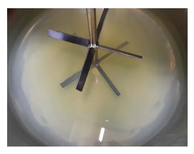
Removal of U in Effluent by meta-Ankoleite formation

- **$KUO_2PO_4(H_2O)_x$** = K^+ + UO_2^{2+} + PO_4^{3-} + xH_2O log K_{sp} = -25.5

Optimized conditions for uranium removal

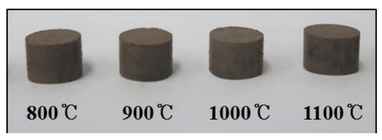
pH	Ion	Dosage	Stir speed	Time	Final [U]
6.0 – 6.5	K^+	2 mM	100 rpm	30 min	20 ppb

(which is below the release limit)

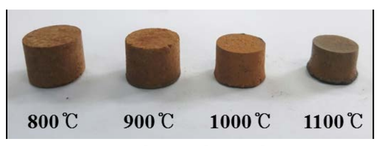


Glass-ceramic solidification of solid waste using B_2O_3

- **Sintering mixture of final solid waste and B_2O_3 at 1100°C**



Green body



After sintering

SiO_2/B_2O_3	Volume reduction (%)	Compressive strength (MPa)	Leachability ($g/m^2 \cdot day$)
70 : 0	3.55	1.548	1.418×10^{-3}
70 : 10	12.45	12.38	1.362×10^{-3}
70 : 15	37.49	65.28	1.063×10^{-3}
70 : 20	51.74	67.85	6.426×10^{-4}

(The sintered material has a very stable form with giving additional volume reduction)

Conclusions

The process suggested was confirmed to reduce ~ 80% of uranium catalyst waste volume with meeting release and clearance requirements of less than 1 ppm for solution and 1 Bq/g for solid.

References

1. K. W. Kim *et al*., "The development of a process for the volume reduction of uranium catalyst waste used for production of acrylonitrile", In Press, (2017).
2. Kane M. Kanematsu et al. "Influence of Phosphate and Silica on U(VI) Precipitation from Acidic and Neutralized Wastewaters", Environ. Sci. Technol., 48, **6097-6106**, (2014).