Feasibility Study for the Recycling of Irradiated Beryllium Reflectors in the Research Reactors

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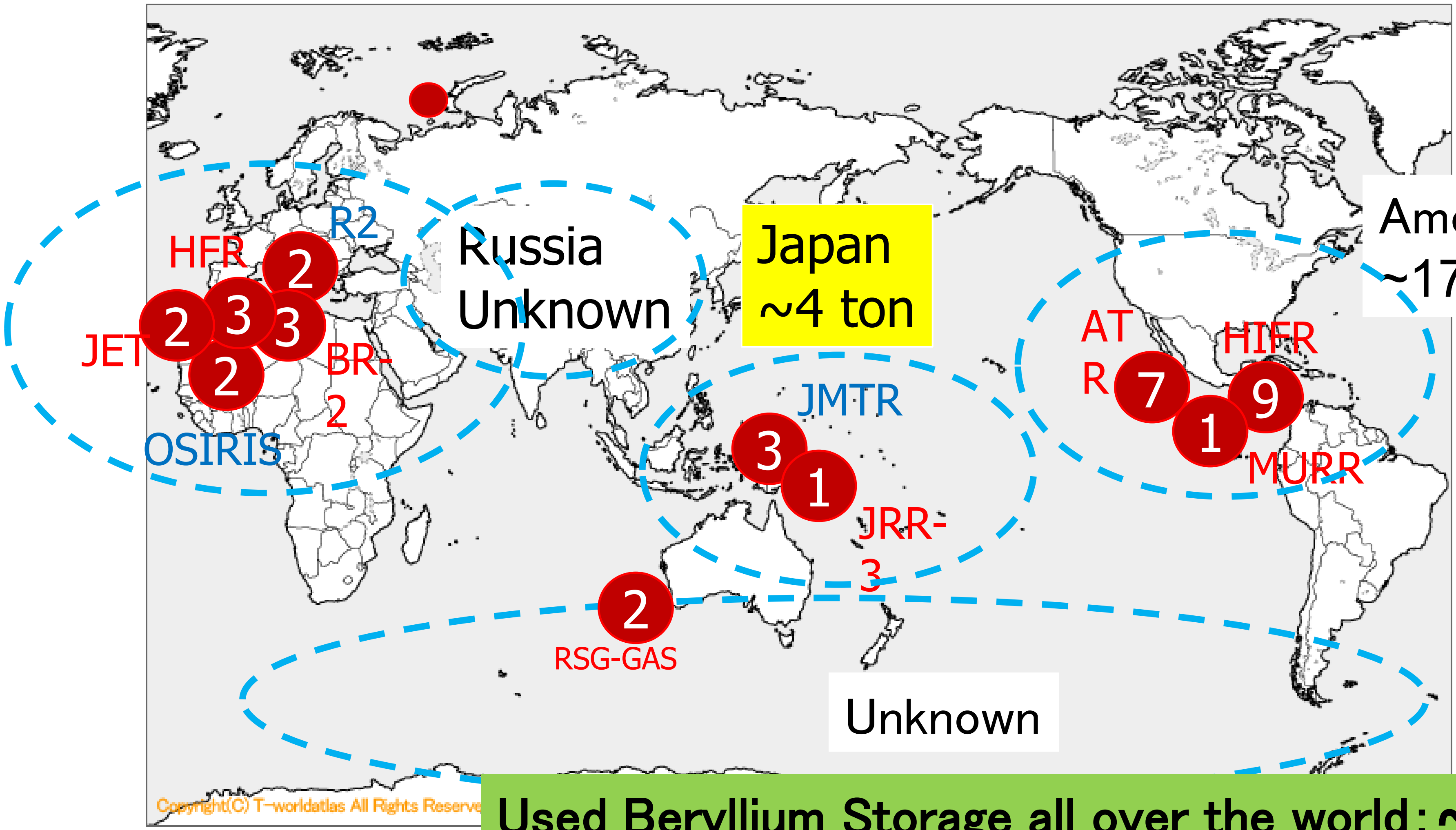
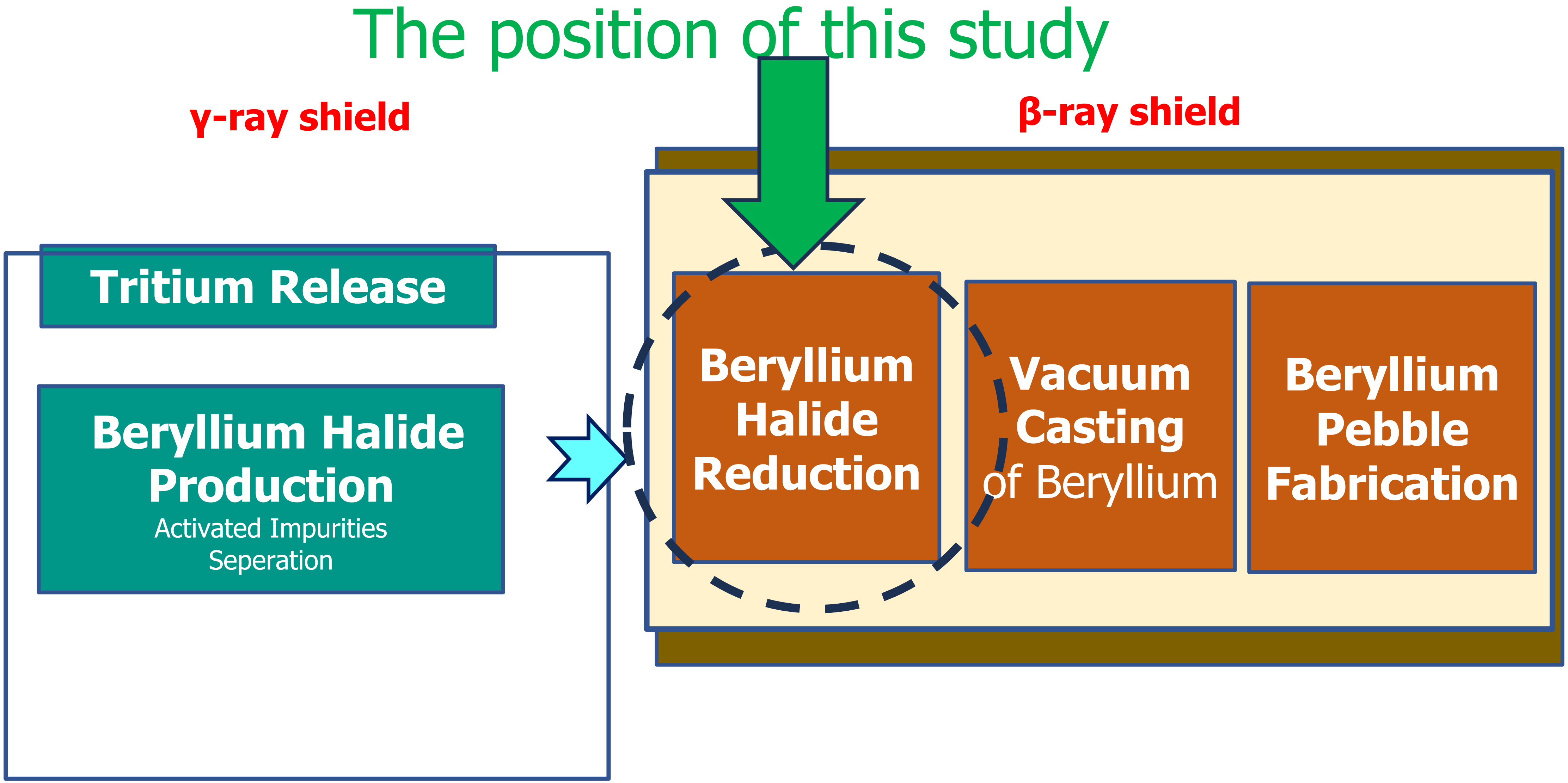


Used Beryllium Storage all over the world ; ~40ton

Technology Stage for Beryllium Recycle



Concept Of this study

Target Beryllium Halide → BeF_2 ,$BeCl_2$,$BeBr_2$,BeI_2

Reduction Method →

①Thermal Decomposition
②Reduction by Hydrogen
③Reduction by Metal
（Na,Mg,Al,Ti,Si,Zr）

Comparison index of reduction methods
1.Chemical Equibrium Constants
2.Partial Pressure of Chemical Products

Comparative Evaluation of Reduction Method

Chemical Equations of Reductiom

Thermal Decomposition

$BeX_2 \Rightarrow Be+X_2$ (X = F, Cl, Br, I)

Reduction by Hydrogen

$BeX_2 + H_2 \quad Be + 2HX$

Reduction by Metal（Mg, Al, Ti, Si, Zr, Na）

$BeX_2 + 2Na \Rightarrow Be + 2NaX$

$BeX_2 + Mg \Rightarrow Be + MgX2$

$BeX_2 + 2/3Al \Rightarrow Be + 2/3AlX_3$

$BeX_2 + 1/2Ti \Rightarrow Be + 1/2TiX_4$

$BeX_2 + 1/2Si \Rightarrow Be + 1/2SiX_4$

$BeX_2 \quad 1/2Zr \Rightarrow Be + 1/2ZrX_4$

Evaluation od Chemical Equilibrium Constants Kc−Value

Chemical Reaction → *a*A + *b*B ⇒ *c*C + *d*D

Chemical Equilibrium Constant → $$K_c = \frac{[C]^c \times [D]^d}{[A]^a \times [B]^b}$$

Kc＝EXP(−ΔG/RT)

Gibbs free energy change：$\Delta G=\Delta H-T\Delta S$

Enthalpy change: $\Delta H=c*H(C)+d*H(D)-a*H(A)-b*H(B)$

Entropy change: $\Delta S= c*S(C)+d*S(D)-a*S(A)-b*S(B)$

H(Z)＆S（Z）：DATA OF NIST

- [Z]:Concentration orof Z

An Example of Kc–Value Evaluation

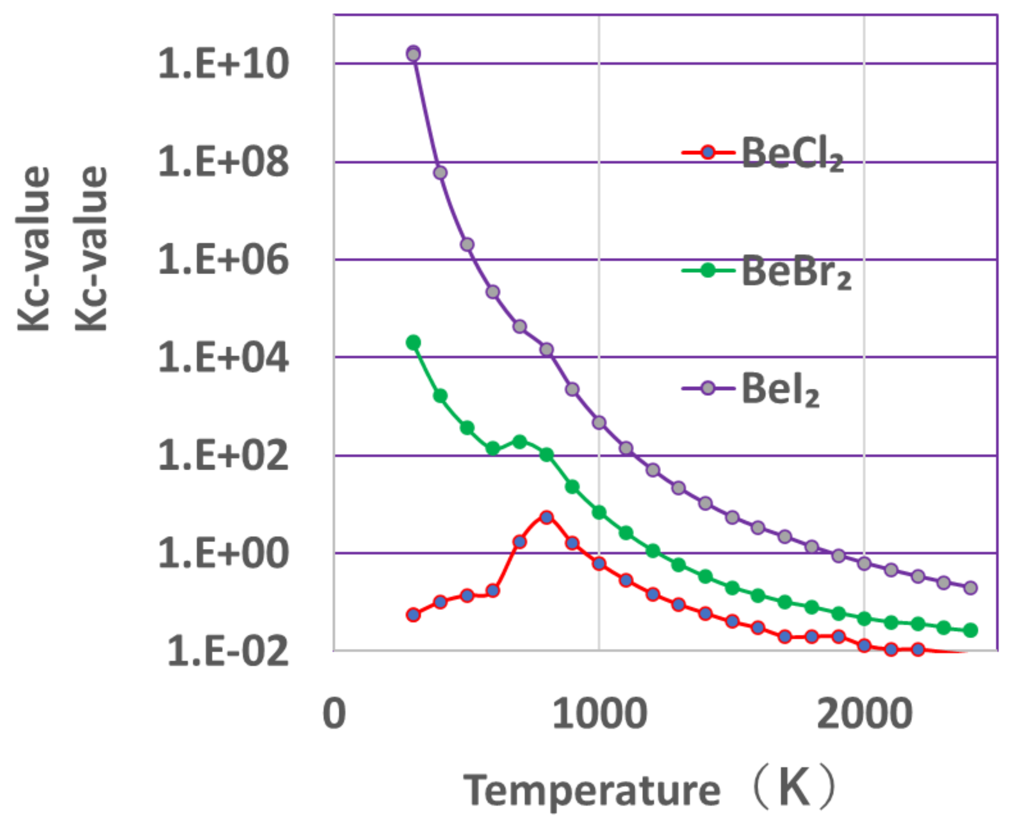
Reduction by Zr

Reduction Equations

$BeCl_2$＋1/2） Zr⇒Be＋(1/2)$ZrCl_4$

$BeBr_2$+(1/2)Zr⇒Be＋(1/2)$ZrBr_4$

BeI_2＋(1/2)Zr⇒Be＋‘(1/2)ZrI_4



Kc-Value of Reduction by Zr

Comparison of *Kc*–Values

Reduction methd	rRank of Kc	MaximumKc	Tempe(K)*	BerylliumHalide	Product ofReductiom
Na	1	2.E+23	900	$BeBr_2$	NaBr
Mg	2	2.E+24	900	BeI_2	MgI_2
Zr	3	2220	900	BeI_2	ZrI_4
Ti	4	0.981	900	BeI_2	TiI_4
Al	5	10.5	900	BeI_2	AlI_3
Si	6	0.0072	800	$BeBr_2$	$SiBr_4$
H2	7	3.E-03	2300	BeI_2	HI
Tharmal Dec.	8	3.E-04	2300	BeI_2	I_2

The **Kc Valuse of Reduction by Na or Mg are very big, but their p It oducts NaX or MgX2 are solid to be separated from Be inside Hot Cell.**

Partial pressure of $AlBr_3$,$TiBr_4$ and $ZrBr_4$ are not comparatively large. By the way, the Melting point of $CoBr_2$ is about 678℃, higher than the Boiling point of $BeBr_2$, 520℃. At the process to make $BeBr_2$, the separation of Co-60 is not so difficult.

Percial Gas Pressures of AlX_3,TiX_4,SiX_4 S i ad ZrX_4 in Reductions are evaluated

The **Kc Valuse of Thermal Deconposition sand Reduction by H2 are very small.**

2. Partial Pressure of Products

Assumptions

$[BeX_2] = p(BeX_2)$: parcial pressure of BeX_2

$[MX_n] = p(MX_n)$: parcial pressure of MX_n

$[M] = [Be] = 1$

$p(BeX_2) + p(MX_n) = 1$ bar(100 kPa)

Chemical Ractions

$BeX_2 + 2/3Al \Rightarrow Be + 2/3AlX_3$

$BeX_2 + 1/2Ti \Rightarrow Be + 1/2TiX_4$

$BeX_2 + 1/2Si \Rightarrow Be + 1/2SiX_4$

$BeX_2 + 1/2Zr \Rightarrow Be + 1/2ZrX_4$

General Expression

$BeX_2 + (2/n)\,M \Rightarrow Be + (2/n)\,MX_n$

$$[Be] * [MX_n]^{(2/n)} = K_c * [BeX_2] * [M]^{(2/n)}$$

Equation of Parcial Pressures

$$p(MX_n) = (K_c * p(BeX_2))^{(n/2)} \qquad K_c = EXP(-\Delta G/RT)$$

$$p(MX_n) + p(BeX_2) = 1 \text{ bar}$$

An Example of Partial Pressure of Products

Reduction by Zr

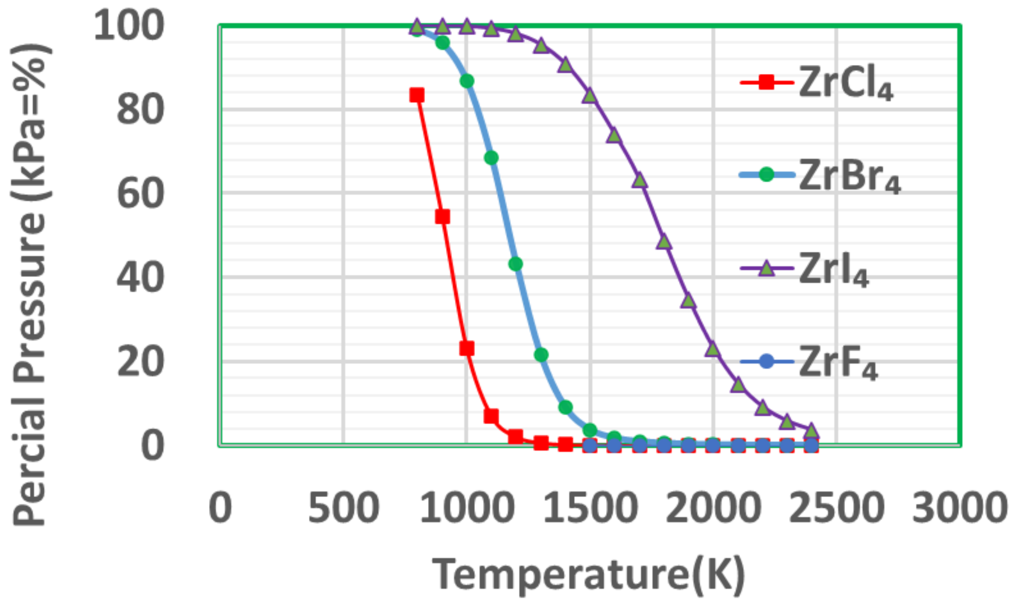
Reduction Equations

$BeCl_2$ + 1/2) Zr ⇒ Be + (1/2)ZrC

$BeBr_2$ + (1/2)Zr ⇒ Be + (1/2)$ZrBr_4$

BeI_2 + (1/2)Zr ⇒ Be + ‘(1/2)ZrI_4

BeF_2 + (1/2)Zr ⇒ Be + (1/2)ZrF



Percial Pressure due to the reduction by Zr

Comparison of Partial Pressure of Products

Table 2-1 Selecting the highest partial pressure for each method

Reduction methd	rRank of P(MXn)	Highest PXn)(kPa)	Tempe (K)*	Beryllium Halide	Product of Reductiom
Zr	1	99.96	900	BeI_2	ZrI_4
Al	2	91.1	900	BeI_2	AlI_3
Ti	3	37.5	900	BeI_2	TiI_4
Si	4	5.35E-04	800	$BeBr_2$	$SiBr_4$

Table2-2 Selecting the second highest partial pressure

Reduction metho	rRank of P(MXn)	2nd Highest PXn)(kPa)	Tempe (K)*	Beryllium Halide	Product of Reductiom
Zr	1	99.07	800	$BeBr_2$	$ZrBr_4$
Al	2	59.9	800	$BeBr_2$	$AlBr_3$
Ti	3	29.62	1100	$BeBr_2$	$TiBr_4$
Si	4	2.8E-08	900	BeI_2	SiI_4

Partial pressure of $SiBr_4$ are very small.

Partial pressure of AlI_3, TiI_4 and ZrI_4 are comparatively large. However, the boiling point of CoI_2 is 570℃, which is lower than that of BeI_2 of 590℃.
At the process to make BeI_2, the separation of Co-60 from BeI_2 may be difficult.

Partial pressure of $AlBr_3$, $TiBr_4$ and $ZrBr_4$, and the Melting point of $CoBr_2$ is 678℃, an and the Boiling point of $BeBr_2$ of 520℃.
At the process to make $BeBr_2$, the separation of Co-60 is not difficult.

Summary(1/2)

1. The equilibrium constants (hereafter referred to as Kc-Value) of the reduction methods for beryllium halides studied in this research, ordered from highest to lowest, are as follows:

   Na > Mg > Ti > Zr > TiAl >> Si > H_2 > thermal decomposition

2. The K-Values for reduction using H_2 or thermal decomposition are extremely low, and practical application is considered infeasible unless the reaction products are actively removed.

3. The Kc-Values for reduction using Na and Mg are extremely high, but unless the process is operated at high temperatures (above 1300° C), the reaction products remain as solids mixed with metallic beryllium.

Summary(2 /2)

4.Based on the results of this study, using $BeBr_2$ and reducing with Zr was evaluated to be the most suitable method among methods studied.

5. For a more accurate selection of beryllium halide Reduction, investigation s are required as follows.

- Chemical reaction rate of the reduction reaction
- Configuration and cost assessment of the reduction apparatus
- Consideration of processes before and after the reduction stage