USE OF THERMODYNAMIC SIMULATION FOR PRELIMINARY STUDY ON ELECTROLYTE RECYCLE PROCESS BY PHOSPHATE CONVERSION TECHNIQUE

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1. Introduction

 * At the Japan Atomic Energy Agency (**JAEA**), as part of our main activity, is to establish the Fast Reactor Nuclear Fuel Cycle for the next power generation system.

 * This project is named **FaCT** (**Fa**st Reactor **C**ycle **T**echnology **D**evelopment), and is designated as one of the national critical technologies.
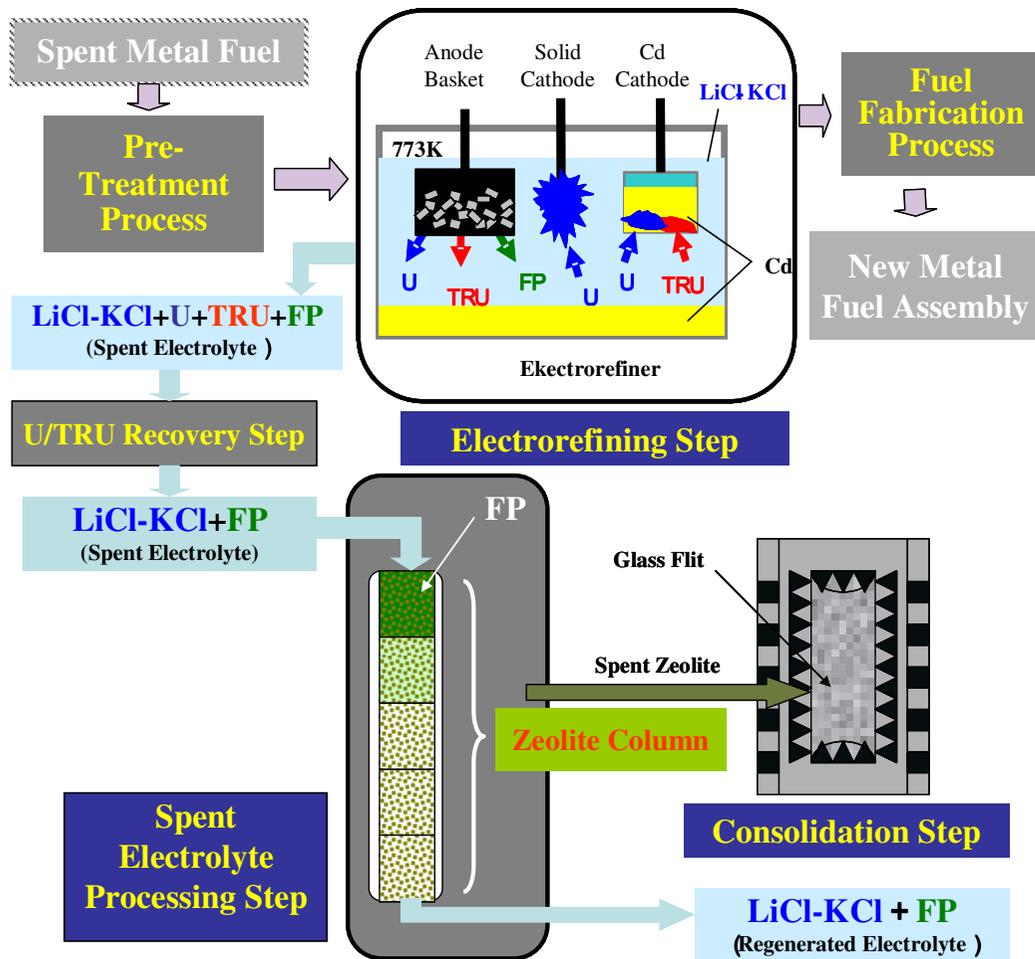

Nuclear Fuel Cycle Systems of LWR and FR
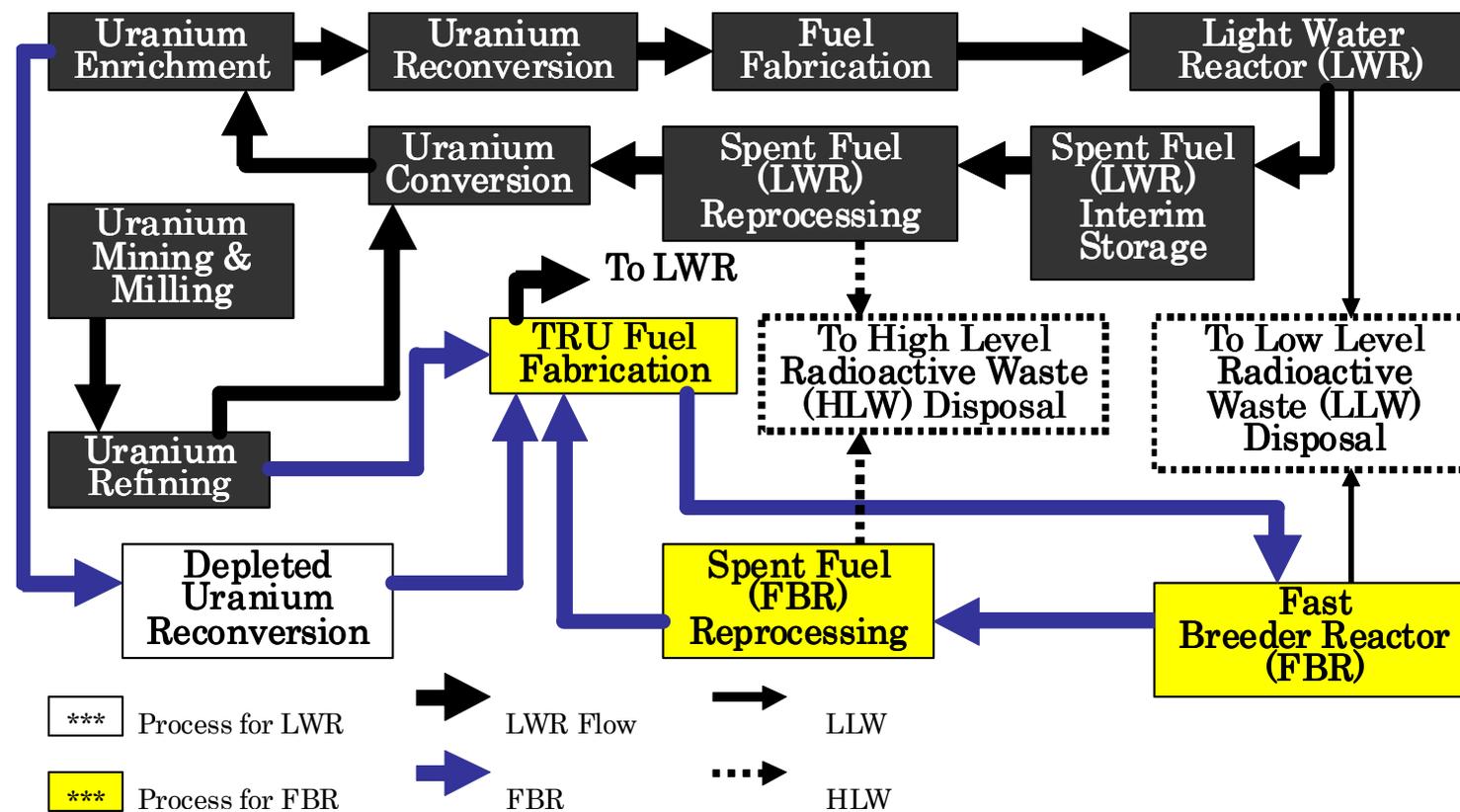
To prepare uranium (U) for use in a nuclear reactor, it undergoes the steps of mining and milling, conversion, enrichment and fuel fabrication. These steps make up the **front end** of the nuclear fuel cycle.

 After U has been used in a reactor to produce electricity it is known as spent fuel and may undergo a further series of steps including temporary storage, reprocessing, and recycling before eventual disposal as waste. Collectively these steps are known as the **back end** of the fuel cycle. These are the various steps that together make up the entire **Nuclear Fuel Cycle**. (World Nuclear Org.)

2. Pyroprocessing in FaCT Project

Spent Metal Fuel

Pre-Treatment Process

Anode Basket · Solid Cathode · Cd Cathode

LiCl-KCl

773K

U · TRU · FP · U · TRU · Cd

Ekectrorefiner

Fuel Fabrication Process

New Metal Fuel Assembly

LiCl-KCl+U+TRU+FP
(Spent Electrolyte)

U/TRU Recovery Step

Electrorefining Step

LiCl-KCl+FP
(Spent Electrolyte)

FP

Glass Flit

Spent Zeolite

Zeolite Column

Consolidation Step

Spent Electrolyte Processing Step

LiCl-KCl + FP
(Regenerated Electrolyte)

Spent Electrolyte Recycle Process

" *Pyroprocessing* " in the FaCT Project is highlighted for this Workshop.

In the FaCT Project, Pyroprocessing by *Metal electrorefining method* is :

• evaluated as *a complementary concept* for FR metal fuel reprocessing;

• based on the application of pyroprocessing *concept of ANL* in the US;

• needed to *recycle its spent electrolyte* after removing the accumulated FP in the light of environmental load reduction and economical improvement.

⇒*The zeolite sorption technique is being developed to regenerate the spent electrolyte.*

The spent zeolite is generated by the break-through of FP sorption.
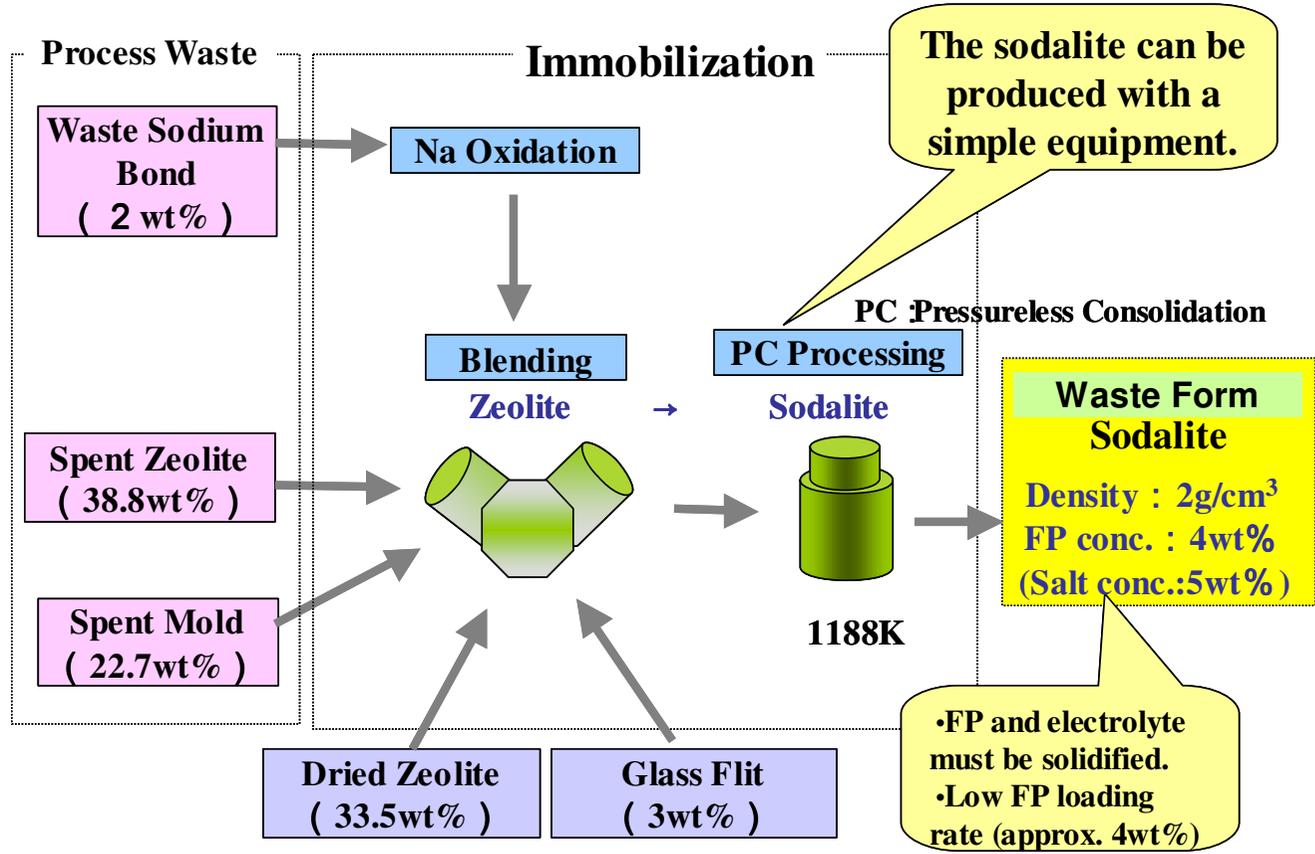
⬇

•**Measures for Immobilization of Spent Zeolite**

⬇

Its Conversion to Soda-lite (Na$_6$[(AlO$_2$)$_6$(SiO$_2$)$_6$]) by Blending, Pressurizing and Heating with Glass Flit, etc..

⬇

Study subject for the realization of zeolite sorption technique

* **Low FP loading rate : approx.4wt%**

* **Generation of a large volume of sodalite as HLW**

Process Waste

Immobilization

| Waste Sodium Bond (2 wt%) | → | Na Oxidation |

The sodalite can be produced with a simple equipment.

PC : Pressureless Consolidation

PC Processing

Blending

Zeolite → **Sodalite**

| Spent Zeolite (38.8wt%) |

| Spent Mold (22.7wt%) |

1188K

Waste Form Sodalite

Density : 2g/cm^3
FP conc. : 4wt%
(Salt conc.:5wt%)

| Dried Zeolite (33.5wt%) | | Glass Flit (3wt%) |

•FP and electrolyte must be solidified.
•Low FP loading rate (approx. 4wt%)

Schematic Diagram on Immobilization of Spent Zeolite

Some measures are necessary to reduce the HLW volume from the viewpoint of environmental load reduction and economical improvement.

5. Phosphates Precipitation Technique

One of the Candidates:

⇒ *Phosphates Precipitation Technique* for oxide fuel which is being developed at *RIAR* (the Research Institute of Atomic Reactors) in **Russia**

⇒Removal of FP （MA,RE) by reaction with Na_3PO_4 and Na_2CO_3

at 973K in NaCl-KCl system electrolyte
or at 923K in NaCl-2CsCl system electrolyte

FP removal efficiency was confirmed by fundamental experiments at RIAR.

Condition for the application of phosphates precipitation technique to the metal electrorefining method
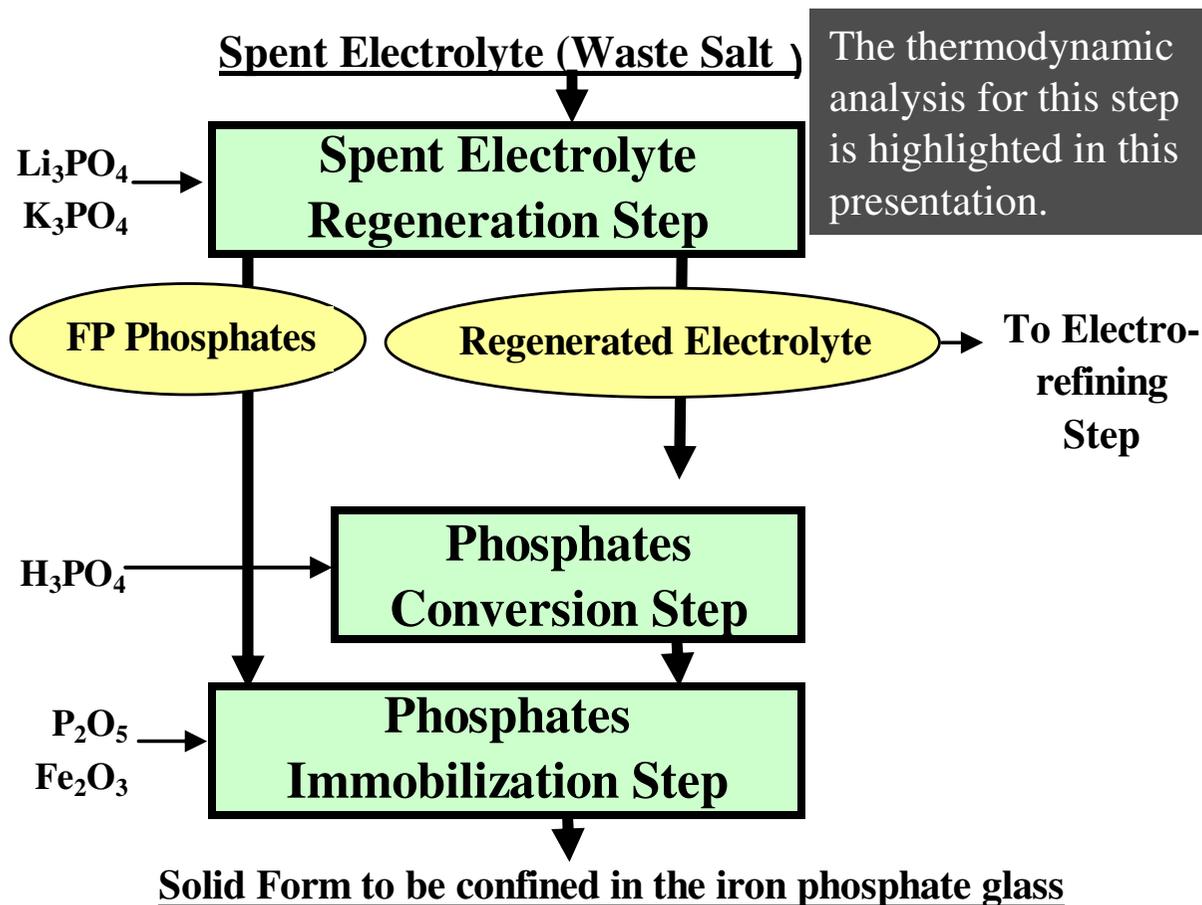(1) Constituent of electrolyte : *LiCl-KCl*
(2) Operational temperature ： *approx.773K*
(3) *Immobilization method* of FP precipitates

In this study, the stable-conditioned iron phosphate glass, developed by Prof.Day of University of Missouri-Rolla in US, is selected for vitrification of FP precipitates.

6. Construction of Conceptual Block Flow Diagram

The conceptual block flow diagram of spent electrolyte recycle process :
- is constructed by applying known results from relevant literature;
- consists of 3 steps, i.e., "Spent Electrolyte Regeneration Step", "Phosphates Conversion Step", and "Phosphates Immobilization Step".

Spent Electrolyte (Waste Salt)

The thermodynamic analysis for this step is highlighted in this presentation.

Li_3PO_4
K_3PO_4 →

Spent Electrolyte Regeneration Step

FP Phosphates

Regenerated Electrolyte → **To Electro-refining Step**

H_3PO_4 →

Phosphates Conversion Step

P_2O_5
Fe_2O_3 →

Phosphates Immobilization Step

Solid Form to be confined in the iron phosphate glass

Conceptual Block Flow Diagram of Spent Electrolyte Recycle Process

Function of Each Step

* **Spent Electrolyte Regeneration Step** is to removes FP as the phosphate precipitates by reaction with some phosphates i.e., Li_3PO_4 and/or K_3PO_4.

* **Phosphates Conversion Step** is to convert the disused electrolyte into phosphates such as Li_3PO_4 and K_3PO_4.

* **Phosphates Immobilization Step** is to vitrify such phosphates formed at the former two steps to be confined in the iron phosphate glass.

Objective

* To evaluate the conceptual block flow diagram, theoretical analysis is important before fundamental experiment.

* The thermodynamic properties for relevant substances are required to conjecture their behaviours.

* Few data exist for relevant phosphates.

* Acquisition of thermodynamic properties, their evaluation, and constructing them as database

Methodology

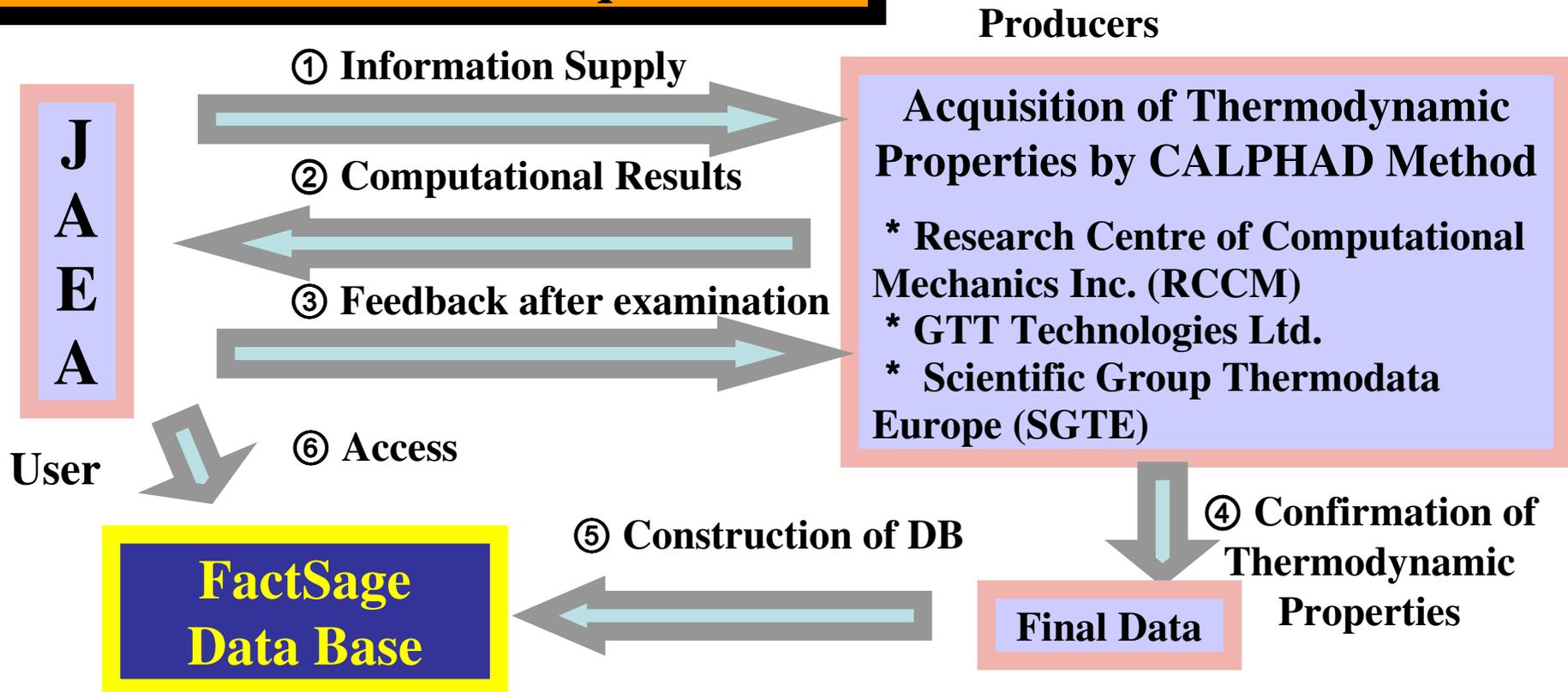* conjecture of thermodynamic properties from known physico-chemical data

* by CALPHAD (CALculation of PHAse Diagrams) method

CALPHAD Method

is to construct the thermodynamic properties, which are consistent with the known data, from the published phase diagrams and relevant physical properties by thermodynamically optimization of data.

Procedure of Data Acquisition

Producers

JAEA

User

① Information Supply

② Computational Results

③ Feedback after examination

Acquisition of Thermodynamic Properties by CALPHAD Method

* Research Centre of Computational Mechanics Inc. (RCCM)
* GTT Technologies Ltd.
* Scientific Group Thermodata Europe (SGTE)

④ Confirmation of Thermodynamic Properties

⑥ Access

⑤ Construction of DB

Final Data

FactSage Data Base

ortho	piro	meta	ortho	piro	meta
Li_3PO_4	$Li_4P_2O_7$	$LiPO_3$	$LaPO_4$	$La_4(P_2O_7)_3$	$La(PO_3)_3$
Na_3PO_4	$Na_4P_2O_7$	$NaPO_3$	$CePO_4$	$Ce_4(P_2O_7)_3$	$Ce(PO_3)_3$
K_3PO_4	$K_4P_2O_7$	KPO_3	$PrPO_4$	$Pr_4(P_2O_7)_3$	$Pr(PO_3)_3$
Cs_3PO_4	$Cs_4P_2O_7$	$CsPO_3$	$NdPO_4$	$Nd_4(P_2O_7)_3$	$Nd(PO_3)_3$
Sr_3PO_4	$Sr_4P_2O_7$	$SrPO_3$	$PmPO_4$	$Pm_4(P_2O_7)_3$	$Pm(PO_3)_3$
$Ba_3(PO_4)_2$	$Ba_2P_2O_7$	$Ba(PO_3)_2$	$SmPO_4$	$Sm_4(P_2O_7)_3$	$Sm(PO_3)_3$
			$EuPO_4$	$Eu_4(P_2O_7)_3$	$Eu(PO_3)_3$
			$GdPO_4$	$Gd_4(P_2O_7)_3$	$Gd(PO_3)_3$
			$TbPO_4$	$Tb_4(P_2O_7)_3$	$Tb(PO_3)_3$
			$DyPO_4$	$Dy_4(P_2O_7)_3$	$Dy(PO_3)_3$

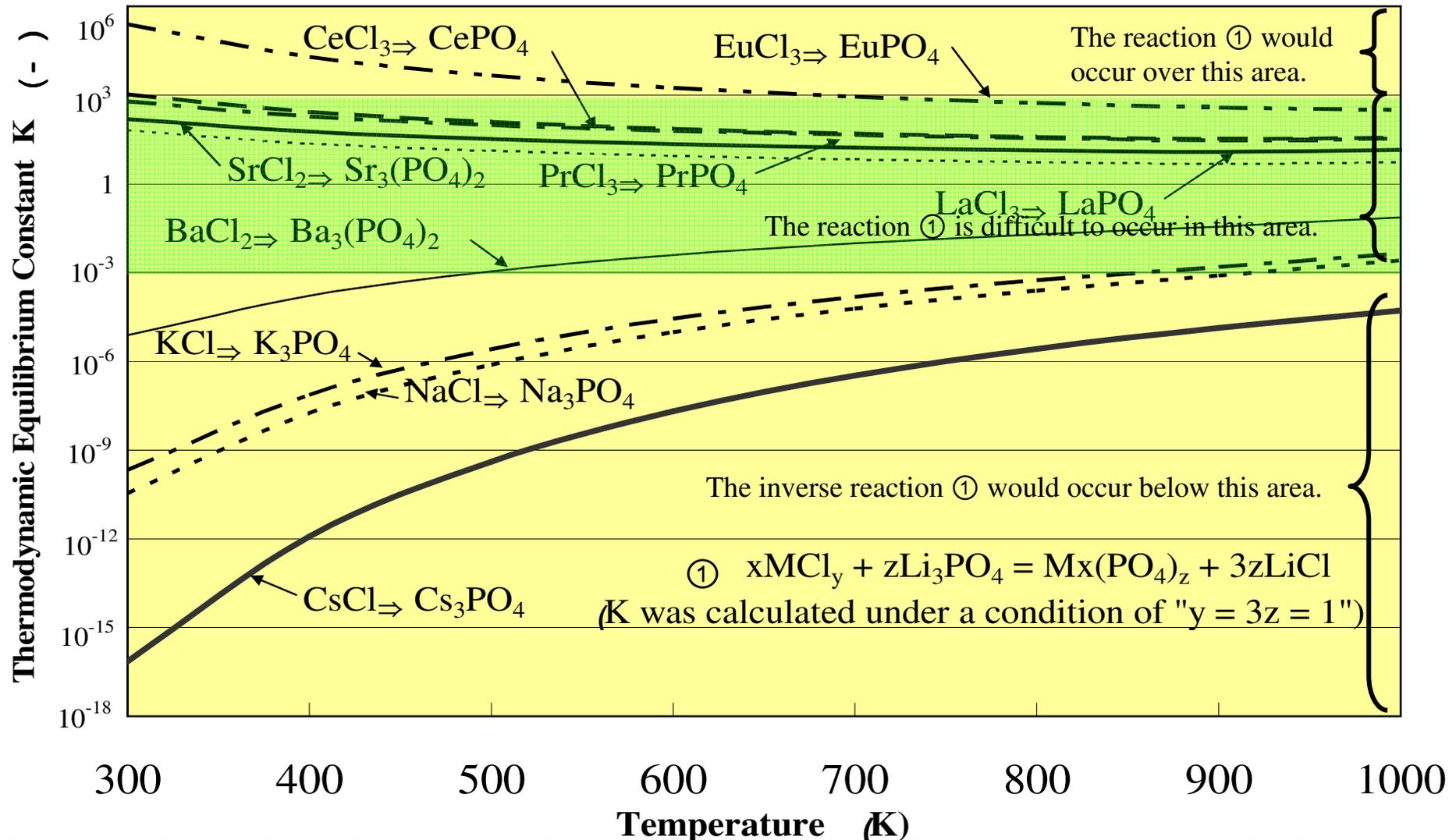**Thermodynamic properties of phosphates such as ortho, piro and meta were obtained from known data.**

* 12 kinds of alkali metal phosphates
* 6 kinds of alkali earth metal phosphates
* 30 kinds of lanthanoids phosphates

Stored in the FactSage Data Base

Thermodynamic Analysis of Phosphate Conversion Behaviour in Electrolyte

Feasibility study of the phosphates conversion of FP chlorides in the electrolyte

Thermodynamic Equilibrium Constant K　(-)

$CeCl_3 \Rightarrow CePO_4$

$EuCl_3 \Rightarrow EuPO_4$

The reaction ① would occur over this area.

$SrCl_2 \Rightarrow Sr_3(PO_4)_2$　$PrCl_3 \Rightarrow PrPO_4$

$LaCl_3 \Rightarrow LaPO_4$

$BaCl_2 \Rightarrow Ba_3(PO_4)_2$

The reaction ① is difficult to occur in this area.

$KCl \Rightarrow K_3PO_4$

$NaCl \Rightarrow Na_3PO_4$

The inverse reaction ① would occur below this area.

①　$xMCl_y + zLi_3PO_4 = Mx(PO_4)_z + 3zLiCl$

(K was calculated under a condition of "y = 3z = 1")

$CsCl \Rightarrow Cs_3PO_4$
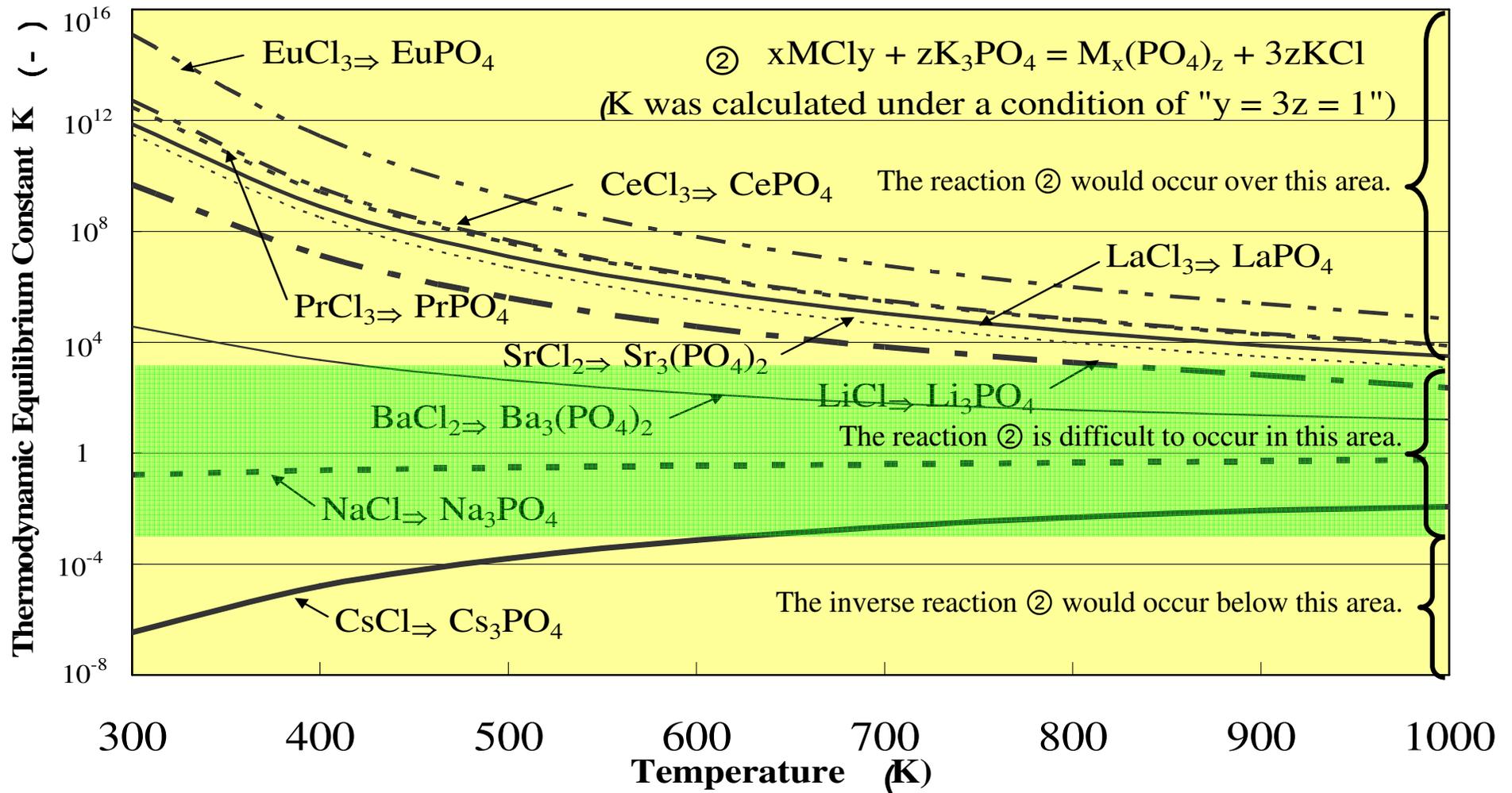
Temperature　(K)

300　400　500　600　700　800　900　1000

Reaction Formula : $xMCl_y + zLi_3PO_4 = M_x(PO_4)_z + 3zLiCl$　　　　Additive : Li_3PO_4

Easy Converting Substances : Lanthanoid (Ln) chlorides, $(SrCl_2)$

Difficult Converting Substances : KCl, NaCl , CsCl , $BaCl_2$

8.2 Calculation　(2)　: Thermodynamic Equilibrium

$EuCl_3 \Rightarrow EuPO_4$

② $xMCl_y + zK_3PO_4 = M_x(PO_4)_z + 3zKCl$

(K was calculated under a condition of "y = 3z = 1")

$CeCl_3 \Rightarrow CePO_4$　The reaction ② would occur over this area.

$LaCl_3 \Rightarrow LaPO_4$

$PrCl_3 \Rightarrow PrPO_4$

$SrCl_2 \Rightarrow Sr_3(PO_4)_2$

$LiCl \Rightarrow Li_3PO_4$

$BaCl_2 \Rightarrow Ba_3(PO_4)_2$

The reaction ② is difficult to occur in this area.

$NaCl \Rightarrow Na_3PO_4$

The inverse reaction ② would occur below this area.

$CsCl \Rightarrow Cs_3PO_4$

Thermodynamic Equilibrium Constant K　(-)

Temperature　(K)

Reaction Formula : $xMCl_y + zK_3PO_4 = M_x(PO_4)_z + 3zKCl$　Additive : K_3PO_4

Easy Converting Substances : $LiCl$, $SrCl_2$, Lanthanoids (Ln)chlorides, ($BaCl_2$)

Difficult Converting Substances : $NaCl$, $CsCl$,

Dosage of Li_3PO_4	LiCl	KCl		CsCl	$BaCl_2$	$SrCl_2$			$LaCl_3$
	(100)	(100)		(1)	(1)	(1)			(1)
Initial Condition (Total Dosage:0mol)	LiCl	KCl	Li_3PO_4	K_2BaCl_4	$CsSrCl_3$	Cs_2BaCl_4	$Sr_3(PO_4)_2$	K_2LaCl_5	$LaPO_4$
	(100)	(96)	(0)	(1)	(1)	(0)	(0)	(1)	(0)
Addtion of 1mol Li_3PO_4 (Total Dosage: 1mol)	(103)	(98)	(0)	(1)	(1)	(0)	(0)	(0)	(1)
Addtion of 0.67mol Li_3PO_4 (Total Dosage: 1.67mol)	(105)	(99)	(0)	(0.5)	(0)	(0.5)	(0.3333)	(0)	(1)
Addtion of 1mol Li_3PO_4 (Total Dosage:2.67mol)	(105)	(99)	(1)	(0.5)	(0)	(0.5)	(0.3333)	(0)	(1)
Addition of 2.33mol Li_3PO_4 (Total Dosage:5mol)	LiCl	KCl	Li_3PO_4	K_2BaCl_4	$CsSrCl_3$	Cs_2BaCl_4	$Sr_3(PO_4)_2$	K_2LaCl_5	$LaPO_4$
	(105)	(99)	(3.3333)	(0.5)	(0)	(0.5)	(0.3333)	(0)	(1)

the unit of the number in the parenthesis : mol

* The reaction products are calculated by the **Gibbs Energy minimization method** under the condition of LiCl - KCl - $FPCl_x$ system as the ideal solution at 800K.

* The **Ln orthophosphates** are formed first, then **Strontium(Sr) orthophosphate** by adding **Li_3PO_4**.

* Other substances are not formed phosphates but double chlorides.

:Starting Material
:Electrolyte
:Phosphate
:Double Salt

8.4 Calculation (4) : Gibbs Energy Minimization

Dosage of K₃PO₄	LiCl	KCl			CsCl	BaCl₂	SrCl₂			LaCl₃
	(100)	(100)			(1)	(1)	(1)			(1)

	LiCl	KCl	Li₃PO₄	K₂BaCl₄	CsSrCl₃	Cs₂BaCl₄	Sr₃(PO₄)₂	K₂LaCl₅	LaPO₄
Initial Condition (Total Dosage:0mol)	LiCl	KCl	Li₃PO₄	K₂BaCl₄	CsSrCl₃	Cs₂BaCl₄	Sr₃(PO₄)₂	K₂LaCl₅	LaPO₄
	(100)	(96)	(0)	(1)	(1)	(0)	(0)	(1)	(0)
Addtion of 1mol K₃PO₄ (Total Dosage: 1mol)	(100)	(101)	(0)	(1)	(1)	(0)	(0)	(0)	(1)
Addtion of 0.67mol K₃PO₄ (Total Dosage: 1.67mol)	(99.99)	(104)	(0)	(0.5)	(0)	(0.5)	(0.3333)	(0)	(1)
Addtion of 1mol K₃PO₄ (Total Dosage:2.67mol)	(97)	(107)	(1)	(0.5)	(0)	(0.5)	(0.3333)	(0)	(1)
Addition of 2.33mol K₃PO₄ (Total Dosage:5mol)	LiCl	KCl	Li₃PO₄	K₂BaCl₄	CsSrCl₃	Cs₂BaCl₄	Sr₃(PO₄)₂	K₂LaCl₅	LaPO₄
	(90)	(114)	(3.3333)	(0.5)	(0)	(0.5)	(0.3333)	(0)	(1)

the unit of the number in the parenthesis : mol

* The reaction products with K_3PO_4 are calculated under the same condition of " Calculation (3)".

* The phosphates conversion behaviours of FP chlorides are the same as that of Li_3PO_4 as the additive.

* The excess addition of K_3PO_4 causes the increase in the amount of KCl and Li_3PO_4 and reduction of LiCl because K_3PO_4 converts LiCl to phosphate.

9.1 Results and Discussion (1) : Comparison with literatures

Constituent	Formula of Precipitate	Remarks
CsCl	unknown	the constituent of electrolyte after experiment ·LiCl ,KCl ,Li_3PO_4 ,Cs_3PO_4
$BaCl_2$	Li_3PO_4 (Ba:5.4wt%)	
$SrCl_2$	Li_3PO_4 (Sr:5.4wt%)	
$CeCl_3$, $Sr/BaCl_2$	$CePO_4$[mon] , Li_3PO_4	· Ce can be removed almost perfectly. · Sr/Ba is difficult to remove. · Removal Rate: 1-3% of Sr ,2-4% of Ba
$ZrCl_4$, $Sr/BaCl_2$	$(Sr/Ba)_2Zr(PO_4)_2$, Li_3PO_4	· Zr can be removed almost perfectly. · Sr/Ba is difficult to remove. · Removal Rate: 3% of Sr ,9% of Ba
$CeCl_3$,$ZrCl_4$, $Sr/BaCl_2$	$CePO_4$,$(Sr/Ba)_2Zr(PO_4)_2$, Li_3PO_4	More than 90% of Ba and Sr do not precipitate.

Operational Temp : 823K

Additive : Li_3PO_4

Molar Ratio of PO_4^{3-}/M^{n+} : approx.5

Constituent	Formula of Precipitate	Remarks
$LaCl_3$	$LaPO_4$[mon] (La:44.2wt%), Li_3PO_4	·Ln chlorides can be converted perfectly with more than 5 mollar ratio of Ln/additive. · The constituent of precipitates is $LnPO_4$ and excess addition of Li_3PO_4.
$CeCl_3$	$CePO_4$[mon] (Ce:60.2wt%)	
$PrCl_3$	$PrPO_4$ [mon] (Pr:38.4wt%), Li_3PO_4	
$NdCl_3$	$NdPO_4$ [mon] (Nd:39.2wt%), Li_3PO_4	
$SmCl_3$	$SmPO_4$ [mon] (Sm:38.3wt%), Li_3PO_4	
$EuCl_3$	$EuPO_4$ [mon] (Eu:53.2wt%), Li_3PO_4	
$GdCl_3$	$GdPO_4$[mon] (Gd:44.1wt%), Li_3PO_4	
$TbCl_3$	$TbPO_4$[tetr] (Tb:35.1wt%), Li_3PO_4	
$DyCl_3$	$DyPO_4$[tetr] (Dy:35.1wt%), Li_3PO_4	

V.A.Volkovich, et al.,J.Nucl.Mater.323[1],pp.49-56

* The Cs presipitate could not be detected but Cs_3PO_4 was found in the bath.
⇒ Different result from the thermodynamic evaluation.

* Most Ba and Sr did not precipitate but formed double phosphates with Zr.
⇒ The thermodynamic data for double phosphates is necessary for next evaluation.

* Ln chlorides were precipitated as phosphates perfectly by excess addition of Li_3PO_4

* The excess Li_3PO_4 was precipitated without any reaction.
⇒ The same behaviours obtained by thermodynamic calculation.

From computational results and literature retrieval:

 ＊ **Li** and **lanthanoid elements** would form the **insoluble phosphates**;

 ＊ other elements such as alkali metal and alkaline metal would not form the phosphates easily.
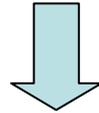
Experimental Results using simple $LiCl$, $CsCl$, $SrCl_2$ or $LaCl_3$ as surrogate FP in $LiCl$-KCl medium.
 ＊ **Li** and **lanthanoid elements** formed the **insoluble phosphates**;
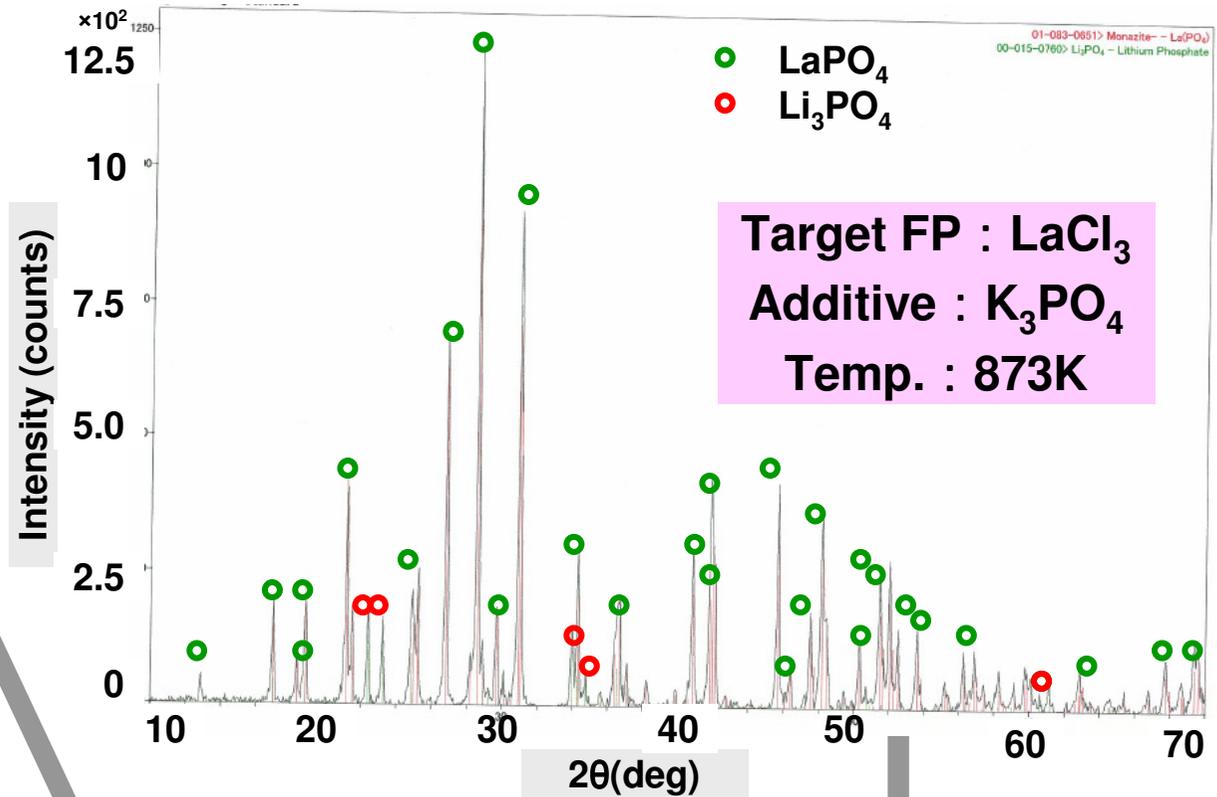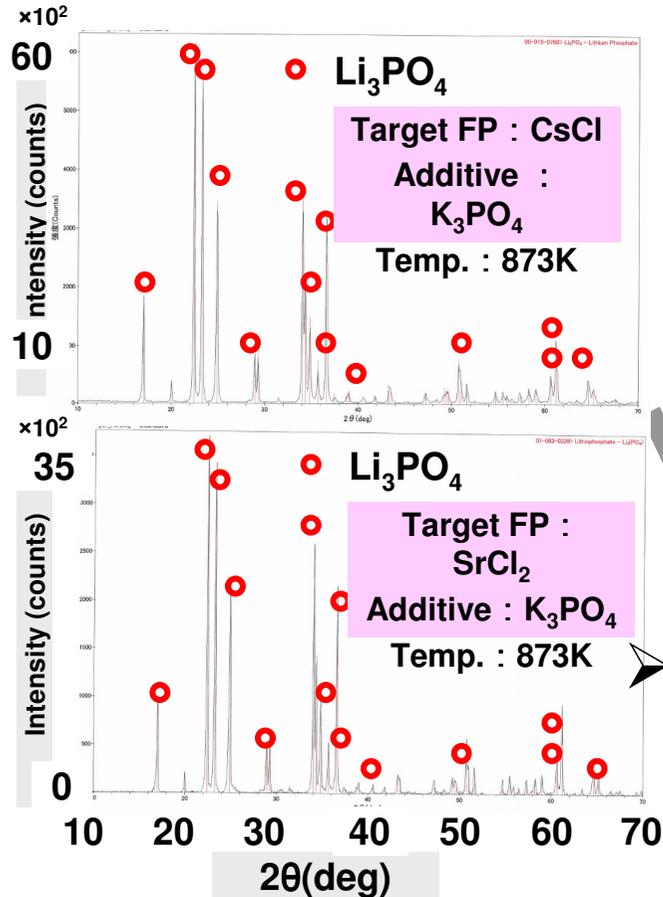
 ＊ other elements did not form the phosphates.
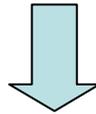
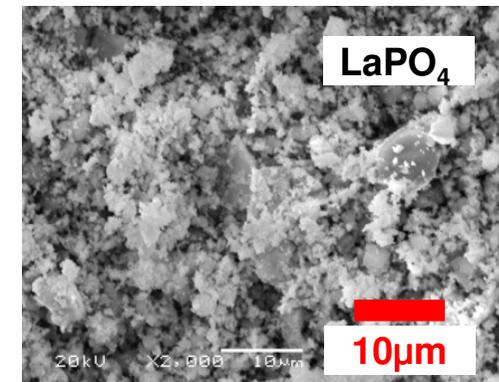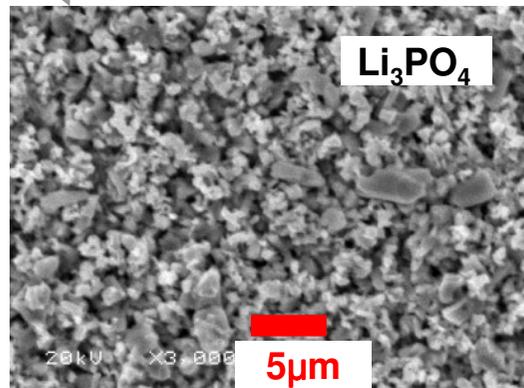**Consilience between computational and experimental results**

➤ Results with XRD

Li and La formed phosphates

Li_3PO_4

Target FP : CsCl
Additive ：K_3PO_4
Temp. : 873K

Li_3PO_4

Target FP : $SrCl_2$
Additive : K_3PO_4
Temp. : 873K

2θ(deg)

○ $LaPO_4$
○ Li_3PO_4

Target FP : $LaCl_3$
Additive : K_3PO_4
Temp. : 873K

2θ(deg)

➤ Observation with SEM

Li_3PO_4

5μm

$LaPO_4$

10μm
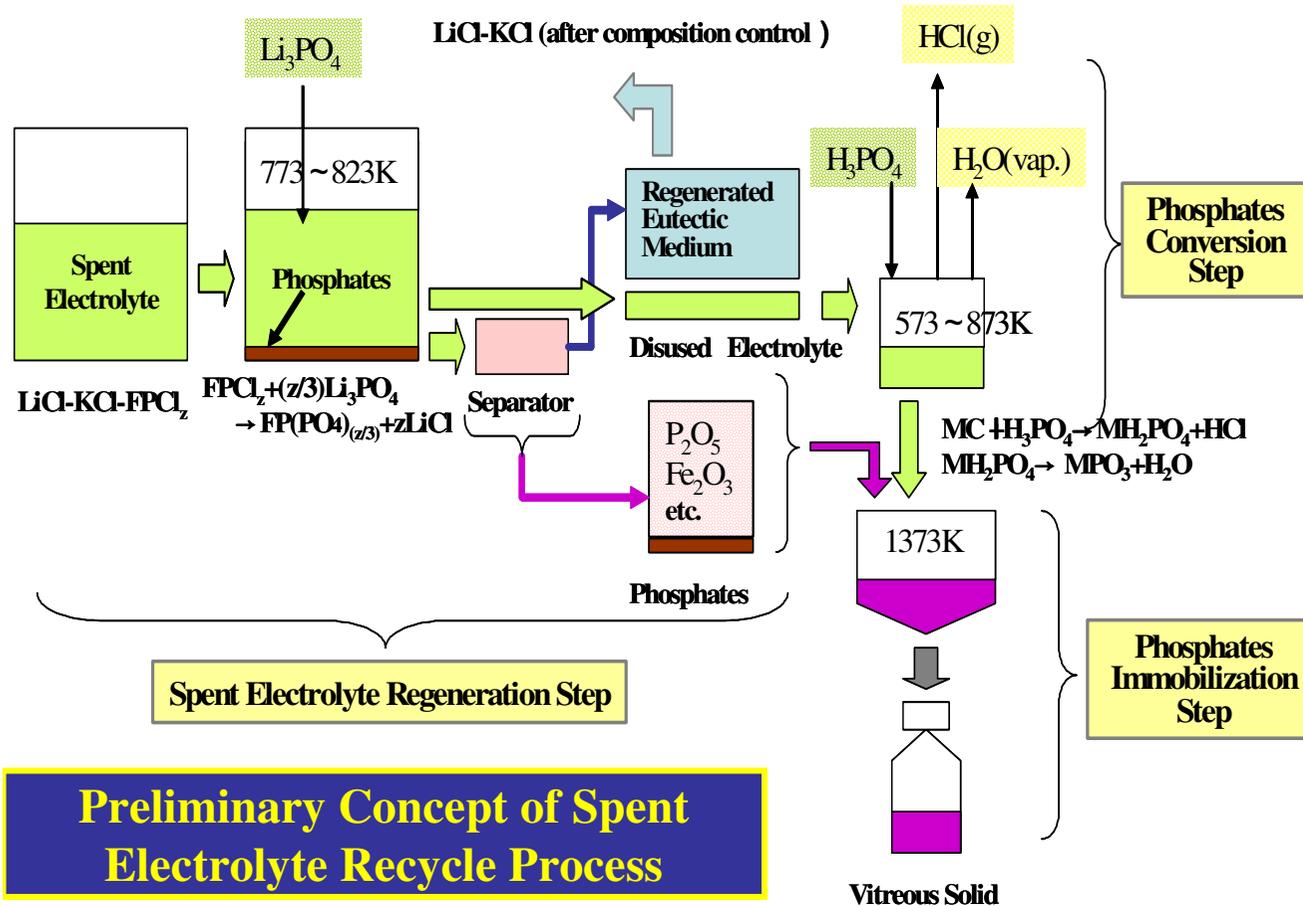
•The major particles of Li_3PO_4 show the micron-size, but sub-micron size of particles could be observed in $LaPO_4$.

Li$_3$PO$_4$

LiCl-KCl (after composition control)

HCl(g)

773~823K

Spent Electrolyte Regeneration Step

H$_3$PO$_4$

H$_2$O(vap.)

Regenerated Eutectic Medium

Phosphates Conversion Step

Spent Electrolyte

Phosphates

Disused Electrolyte

573~873K

LiCl-KCl-FPCl$_z$

FPCl$_z$+(z/3)Li$_3$PO$_4$ → FP(PO4)$_{(z/3)}$+zLiCl

Separator

P$_2$O$_5$ Fe$_2$O$_3$ etc.

MC +H$_3$PO$_4$→ MH$_2$PO$_4$+HCl
MH$_2$PO$_4$→ MPO$_3$+H$_2$O

Phosphates

1373K

Phosphates Immobilization Step

Spent Electrolyte Regeneration Step

Preliminary Concept of Spent Electrolyte Recycle Process

Vitreous Solid

Spent Electrolyte Regeneration Step

*The FP mainly Ln chlorides in the electrolyte can be separated to convert the insoluble phosphates.
*Li$_3$PO$_4$ was recommended as an additive in this study.
*The precipitates and insoluble substances would be recovered by the separator which could function as a molecular sieve and/or a cation exchanger .

Phosphates Conversion Step

*Disused electrolyte is converted to phosphates.
*The two-step conversion is applied to reduce the generation of hydrocloric gas, i.e., first, the generation of hydrogen chloride which is known as relatively inactive gas at around 520-530K, then meta-phosphate and H$_2$O could be obtained by decomposition of dihydrogen phosphate at above 530K.

Phosphate Immobilization Step

*The iron phosphate glass, its expected loading capacity is approx.35% of precipitates, is applied for the immobilization of FP phosphate.

10. Conclusions

*The electrolyte recycle process was suggested as one of the methods to regenerate the spent electrolyte arising from the pyrochemical process by electrorefining method.

*The conceptual block flow diagram was constructed to evaluate its feasibility. Its construction was based on literature search and the thermodynamic properties of target phosphates were acquired by the CALPHAD method.

*Obtained diagram and thermodynamic data should be reinforced by carrying out further accurate evaluation for the next step.

*We require more data derive not only from calculation but experiments too, for verification of theoretical validity and for realization of this process.

*Its materialization in turn, would contribute towards the reduction of HLW.