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A DEVELOPMENT AND AN APPLICATION OF MIXSET-X COMPUTER CODE FOR SIMULATING THE PUREX SOLVENT EXTRACTION SYSTEM

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ABSTRACT

MIXSET[1] is a FORTRAN code developed to simulate the PUREX solvent extraction system using mixer-settler extractors. Japan Nuclear Cycle Development Institute (JNC) has been developing the MIXSET code since the 1970's to analyze the behavior of nuclides in the solvent extraction processes in Tokai Reprocessing Plant (TRP). This paper describes the history of MIXSET code development, the features of the latest version, called MIXSET-X and the application of the code for safety evaluation work.
Keywords: Reprocessing, PUREX Solvent Extraction, Computer Simulation Code, Mixer-Settler, Safety Evaluation

1- INTRODUCTION

Recently power companies tend to introduce high burn-up and utilization of plutonium for fuel. The behavior of long-lived nuclides has been focused on because high burn-up or MOX fuels has more amount of long-lived nuclides than current fuels.

It is important to predict the behavior of the nuclides in the solvent extraction process and the waste handling process. Numerical computer simulation is one of the effective methods to predict the nuclides behavior quantitatively.

The MIXSET code was developed in the 1970's in order to perform the analysis of operational data accumulated in TRP. Then, MIXSET code has been used with some revisions, such as additions of the handling ingredients, distribution coefficients, and chemical reaction formulas in order to carry out the necessary technical study of the solvent extraction behavior of the nuclides in TRP.

In previous version of MIXSET, it was difficult to predict the notable nuclides behavior such as Np,Tc,Pu because of their complicated reaction mechanism. Also, as a result of repeated additions of calculational functions, the program structure became complicated and calculation troubles happened in the case of some combinations of calculation options. Therefore we renew the entire code to adopt new numerical method and new calculation options which enable to various reprocessing process calculations for the current and future processes of TRP.

Though the new code, called MIXSET-X was developed for the JNC's solvent extraction processes with mixer-settler extractors, it can also apply to general PUREX solvent extraction processes.

2- PURPOSE AND HISTORY OF MIXSET-X DEVELOPMENT

MIXSET has been revised several times. The original MIXSET code was developed in 1977. It simulates the solvent extraction behavior of only four ingredients chosen from total of eight ingredients, such as U and Pu. " Revised MIXSET[2] " code was developed in 1979. In addition to the solvent extraction simulation, the code can simulate chemical reactions in the extractors by incorporating seven chemical reactions and reaction rate formulas. " Advanced MIXSET[3] " code was developed in 1981. TRU nuclides, such as Am, Cm and Np were newly added to be handled. Those distribution coefficients were formulated based on literature data, etc.

The original MIXSET, Revised MIXSET and Advanced MIXSET codes were all operated on the mainframe computer at that time. In 1996, considering the operability of code handling and maintenance,-" MIXSET-98 " code was developed. The code was converted from " Revised MIXSET ", and was operated in personal computer. Ten Fission Products (FPs) were added to be handled. The code can treat total of 23 ingredients, and 8 chemical reactions.

MIXSET-X[4] was developed in 1999 and it can deal with 31 ingredients, and builds in 45 chemical reaction formulas based on the literatures data. Moreover, it can calculate the solvent degradation using the decay heat data of nuclides.

3- CHARACTERISTICS OF MIXSET-X

The characteristics of MIXSET-X are as followings.

1) Simulation of the behavior of Np, Tc as interactive ingredients. Those nuclides are important in long-term waste management or corrosion management of the process. The" interactive" means that the

concentration of the ingredient affect chemical reaction rate or solvent extraction distribution coefficients of other interactive ingredients.

2) Handling of Pu (V) and Pu (VI) as newly additioned interactive ingredients. Though the previous MIXSET could not treat complicated system including Pu(V) and Pu(VI), they are built in MIXSET-X as interactive ingredients.
3) Thirty-one ingredients such as actinides and fission products are handled. (U(IV), Pu(V), Pu(VI), Np, Ru, Cs, Tc, Zr, nitrous acid etc..)
4) Forty-five chemical reaction formulas including Np,Tc which is built in based on literature data available. (Decomposition reactions, Oxidation-Reduction reactions and so on.)
5) Users can select any distribution coefficients and chemical reactions to be handled. Also users can adjust each reaction rate constant as user's input parameter.
6) Calculation for the process including cycle flow to the upper extractor's bank or stage through buffer tanks is available by introducing the simple buffer tank option. Now, it can calculate the whole extraction process of TRP in one calculation run.
7) TBP degradation calculation can be treated by using the decay heat data of nuclides.
8) New parameters for stage extraction efficiency are available.
9) Only transient calculation can be carried out in this code and the steady state calculation substitutes can be obtained as the result of long-time transient calculation.

4- VALIDATION OF MIXSET-X.

Benchmark calculations were made for MIXSET-X by comparing calculated results with operational data in the solvent extraction process in TRP. Since only transient calculation is possible in MIXSET-X, transient calculation result after 5000 hours was compared with the steady state operational data. The comparison results are shown in Table-1.

Though some differences were observed between the calculation results based on the KfK data[5] and Hanford data[6] for distribution coefficient, they agreed approximately with operational data. In this paper, only 3 ingredients (U,Pu,HNO_3) were compared. We will verify the calculation accuracy for other ingredients through the comparison of TRP operational data in the future.

5- APPLICATION OF MIXSET-X FOR SAFETY EVALUATION WORK

MIXSET-X was first applied to the TRP's safety evaluation work[7].

Through the investigation of the cause of the fire and explosion incident at Bituminization Demonstration Facility in TRP happened in 1997, the lesson learned is that the safety assessments are necessary even for the licensed facilities using recent knowledge. Therefore the safety assessment has been made for the facilities in TRP using recent knowledge and operational experience.

We considered causes of potential hazards as initial events extracted by using HAZOP study that is generally used for identifying hazards and problems. Then we developed event progression after the initial event considering countermeasures for incident prevention. We estimated final result of event progression on the assumption that all incident prevention systems didn't work. When we evaluated event progression quantitatively, we carried out calculations for transition of U, Pu and nitric acid concentration in equipment to judge the possibility of Pu-polymer formation.

Since the MIXSET-X can simulate the operation state different from a normal operation by changing the flow rates of process solutions or reagents, MIXSET-X was used for quantitative evaluation of event progression and played a great role in the assessments.

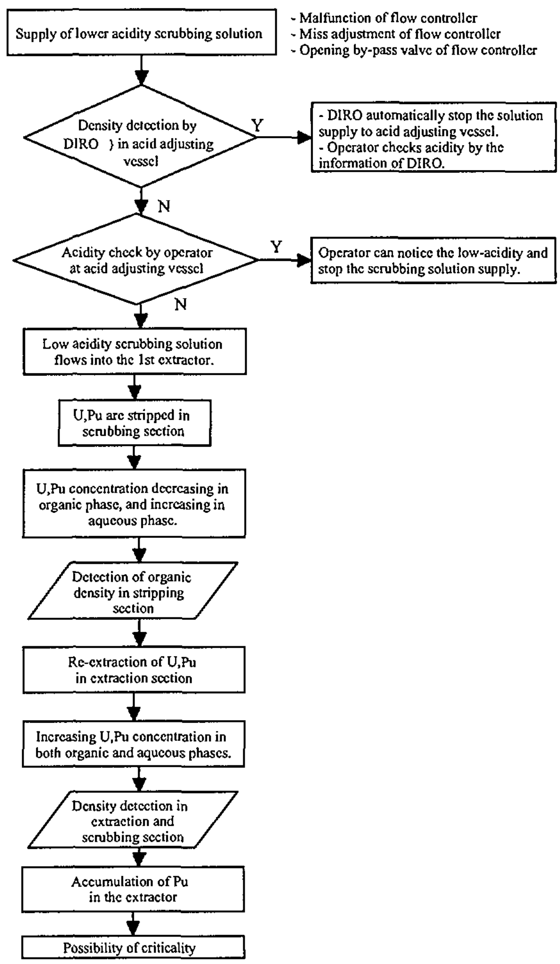

Fig.1 Example of the progression flow chart of the 1st separation cycle

Table-1 Comparison of MIXSET calculation result and operational data

Extraction cycle	Extractor No.	phase	TRP operation data U(g/L)	TRP operation data Pu(g/L)	TRP operation data H+(M/L)	MIXSET-X KfK data U(g/L)	MIXSET-X KfK data Pu(g/L)	MIXSET-X KfK data H+(M/L)	MIXSET-X Hanford data U(g/L)	MIXSET-X Hanford data Pu(g/L)	MIXSET-X Hanford data H+(M/L)
1st	1	aqueous exit	<0.01	<5.0E-05	2.95	N	N	2.72	N	N	2.72
(Co-extraction)	1	organic exit	90.0			90.67	0.68	0.22	90.67	0.68	0.22
	2	aqueous exit	74.0	0.56	0.32	72.88	0.55	0.28	72.88	0.55	0.28
	2	organic exit	<0.01	<5.0E-05		N	N	4.38E-04	N	N	2.35E-04
2nd	3	aqueous exit	<0.01	<5.0E-05	3.07	N	N	2.80	N	N	2.80
(U-Pu separation)	3	organic exit				73.51	0.55	0.31	73.51	0.55	0.31
	4	aqueous exit	8.8	1.64	1.26	2.04	1.62	1.15	3.42	1.62	1.14
	4	organic exit	62.0	<5.0E-05		63.45	N	0.019	63.38	N	0.018
	5	aqueous exit	53.0	<5.0E-05	0.046	52.91	N	0.035	52.85	N	0.034
	5	organic exit				N	N	4.34E-04	N	N	2.32E-04
U-purification	6	aqueous exit	<0.01	<5.0E-05	1.56	0.01	N	1.46	0.03	N	1.47
	6	organic exit				74.46	N	0.01	74.34	N	0.01
	7	aqueous exit	55.0	<5.0E-05	0.03	53.19	N	0.03	53.10	N	0.03
	7	organic exit	<0.01	<5.0E-05		N	N	4.31E-04	N	N	2.30E-04
Pu-purification	8	aqueous exit	<0.01	1.0E-04	4.15	N	0.00	3.91	N	0.00	3.91
	8	organic exit				6.26	4.98	0.20	10.49	4.98	0.19
	9	aqueous exit	<0.01	12.0	1.1	0.00	10.97	0.80	1.81	10.97	0.79
	9	organic exit	24.0	<5.0E-05		16.63	N	0.042	19.32	N	0.032

;"N" shows less than 1.0E-06

For example, we assumed a mal-operation in the chemical reagent preparing system as an initial event. And then it caused low acidity of the scrubbing solution to be supplied to the extractor. Low acidity lead to Pu accumulation in the extractor and it might result in a criticality accident (see fig.1). To estimate the possibility of criticality in extractors, we applied MIXSET-X to calculate the transient concentration of U, Pu and nitric acid. We performed calculation in case of supply of the scrubbing acid solution with unusually low concentration. Calculation conditions are shown in Table-2.

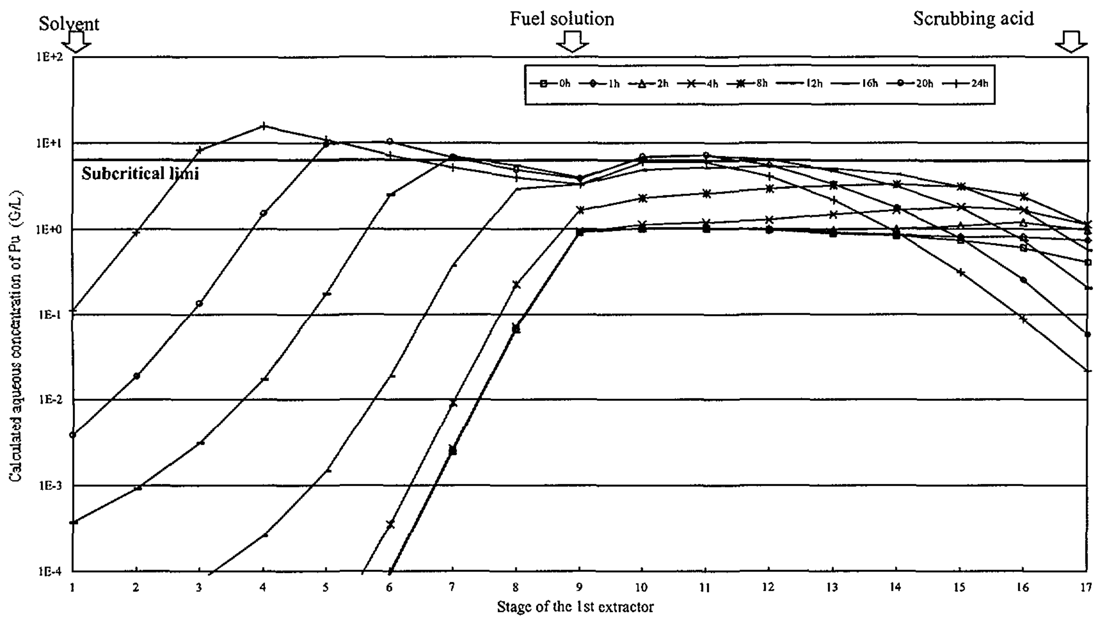

Fig.2 Transient profile of Pu concentration in the 1st extraction process.

Fig.2 shows calculated Pu concentration profiles of aqueous solution at various times up to 24 hours. Possible criticality due to the Pu accumulation in the mixer-settler was pointed out because the Pu concentration exceeded subcritical limit of concentration in the mixer-settler, after about twelve hours.

A lot of evaluation was performed for the whole extraction process. We examined about 1000 cases of abnormal conditions. And there were 20 cases with possibility of criticality as a result of quantitative evaluation using MIXSET-X.

As mentioned above, we checked sufficiency of the incident prevention systems or procedures, and if there were not enough prevention systems or procedures to stop or interrupt event progression, we provided additional incident prevention system or procedures.

6- CONCLUSION

We have developed MIXSET-X which is able to simulate transient solvent extraction behavior of nuclides. In order to verify the calculation accuracy, we compared calculation results with operational data of TRP. The comparison gave good agreement each other. MIXSET-X was applied to safety evaluation work for TRP, and it played the important role in quantitatively evaluation.

7- FUTURE STUDY

We will continue to verify the accuracy of the calculation result by comparison with the operational data or experimental data. Major evaluation items are given below.

- Extraction of Np by changing valency
- Co-extraction of Tc with U, Pu and Zr
- Extraction of Pu (VI) which has complicated reaction
- The validation of a solvent degradation calculation

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