

**PUREX PROCESS EXTRACTION CYCLES :  
A POTENTIAL FOR PROGRESS TODAY ?**

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The Purex process very quickly and very widely supplanted the other concepts considered for nuclear fuel reprocessing after the presentations made at the Geneva Conference in 1955 [1]. The selectivity and radiolytic stability of tributylphosphate (T.B.P.) clearly appeared to augur an extremely attractive process for completing the separation of valuable elements in the irradiated fuel.

The concept has confirmed its validity, and subsequently its ability to adapt to changing requirements or constraints. Its industrial viability is in fact unquestioned today : the Purex process is the basis of all the reprocessing plants in operation or planned throughout the world, and the recent commissioning of the UP3 plant in France, in remarkable conditions [2-3], attests to such a level of maturity that one is tempted to ask the question : "What remains to be proved, discovered or improved in the core of the Purex process ?"

**1 EVOLUTION OF THE PUREX PROCESS FROM THE 1950s TO THE 1980s**

The Purex process has evolved in the last three decades to meet the changing needs successively expressed, from the early recovery of material for defence purposes, to the reprocessing of fuels from nuclear power reactors. This evolution of the context was essentially reflected, in terms of process implementation, by an increasingly "industrial" approach. Major development efforts now are aimed to contend better with reliability, cost and safety concerns, criteria that need to be optimized in an industry that is reaching maturity.

But beyond the growing weight of these considerations, the Purex process had to offer significant progress to meet the need for higher reprocessing capacity, and for lower wastes generation, and, above all, the significant changes in the characteristics of the irradiated fuels to be reprocessed.

Tables 1-2 give figures, from the french experience, that serve to indicate the scale of the adaptation effort that proved necessary. This had to cope with several factors :

- the increase in the quantities of plutonium present in the irradiated fuel : a few parts per thousand for the original Gas Cooled Reactors, typically 1 % for the Light Water Reactors, and about 10 % for the precursors of the Fast Breeder Reactors. Problems of chemical or radiolytic instability and criticality were posed with greater sharpness, leading to developments in the structure of the process (choice of a branched aliphatic diluent, more resistant to  $\alpha$ -radiolytic aggression, for example), and also in the nature and the characteristics of the contactors used for its operation (centrifugal extractors, cylindrical or annular pulsed columns).
- more generally, the significant increase in the burnup of the fuels : the reference irradiated fuel for the french UP3 plant at La Hague thus contains about 4 kg of zirconium and 2 kg of ruthenium per ton of uranium. Apart from their singular extraction behaviour, these elements contribute substantially to the problem of "cruds", which has become increasingly important, and which has also led to changes in extraction equipments.

As the century comes to a close, the industrial achievements in Japan (Rokkasho Mura), the United Kingdom (Sellafield), and France (La Hague), confirm (or very likely will confirm) again advances in the mastery of the Purex process core and in its operation conditions. Every new reprocessing plant, since the end of 1950's, was an opportunity for progress and represented a major step in the development of the Purex process. Thus, the decontamination level reached today in the first extraction cycle of the UP3 plant validates the concept of reprocessing with a reduced number of unit operations. Similarly, the recent achievements testify expertise concerning a number of thorny aspects : the behaviour of certain fission products or actinides (technetium, neptunium) has been clearly pinpointed (and even modelled with striking reliability and accuracy), the problems encountered at the beginning in the use of pulsed columns (axial mixing, "channelling" in the annular sections, change in performances, ...) have essentially been surmounted, and, as demonstrated by the operation of the UP3 plant, the addition of solvent regeneration by distillation represents a considerable advance, both in terms of extraction cycle performance, and in terms of the organic liquid wastes generated.

## 2. GUIDELINES FOR PROGRESS TODAY

The outlook for progress in the core of the Purex process can be considered today along four main guidelines : **better mastery, adaptation, improvement and completion.**

1°/ The idea of better mastery of the process derives from the finding that some aspects are not yet perfectly under control, or at least that the solution that has effectively been found for certain problems does not necessarily demonstrate complete control over the mechanisms concerned. Thus ruthenium decontamination has constantly been improved, but ruthenium remains the major contaminant in the products after the first extraction cycle, and the elementary mechanisms that govern its metabolism are still not perfectly mastered.

From another standpoint, the delicate problem of pulsed columns design has been resolved, certainly with assurance, but at the cost of many applications, studies and tests, sometimes full-scale. The models available for this aspect, although already quite effective in several cases, still appear to be insufficiently reliable if one deviates from the specific field for which they have been developed and validated, then difficult to use for further design.

Thus it appears that continued basic research in Purex related areas connected with chemistry and chemical engineering is a major guideline for progress, both for better control of the plants today under operation and for the preparation of future achievements.

2°/ The Purex process will have to be adjusted to changes in the fuels to be reprocessed. This trend, already discussed above in glancing at the past decades, will obviously continue, and recent reprocessing plants, especially those currently under construction, will have to contend with these developments.

Most of the main lines are clearly identifiable today : the growing importance of plutonium fuel (MOX in LWR and FBR reactors), the increased burnup, the advent of new matrices. While the priority and essential objective is the adjustment of the head-end process, some of these developments are undeniably liable to affect the extraction process, for example, by exacerbating the problems of radiolysis or certain mechanisms inherent in the chemistry of plutonium or certain fission products (see Table 3). In this respect, all the efforts mentioned above, aimed to enhance the control of the elementary mechanisms involved, will naturally contribute to a better approach of this adaptability and to the necessary flexibility that is being sought (perhaps opening up even further prospects, such as the "extended application" of the Purex process in areas allied to reprocessing). However, it will also very probably be necessary to validate the overall feasibility of the treatment for different identified "steps".

Another trend, to be considered yet appearing less established today, could reside in the shortening of interim storage periods for decay before reprocessing. The problems raised in extraction operations would essentially be similar to the earlier ones, although of different origins and application points. The limits of the process would also be set by the conditions of degradation of the solvent, here in the first extraction cycle. Beyond basic research, applicable studies should be initiated too, taking account of the variety of the species present, and also of the main characteristics of the extractors employed.

3°/ Over and above the need for better control and adaptability, the effort to improve the Purex process appears to concern less the search for an overall rise in performance (the degree of purification and the recovery rate of uranium and plutonium globally achieved are today quite satisfactory) than the attainment of the same performance level at lower cost and for a smaller volume of wastes generated.

Investment costs for extraction facilities in reprocessing plants can be cut in various ways. The first is obviously the reduction in the number of purification cycles required to achieve the separation specifications. If the first cycle is efficient enough, the downstream cycles can be eliminated as unnecessary (see Table 4). This is the concept that the German researchers have named IMPUREX (IMproved PUREX) [4], which entails :

- . the optimization of all the elementary processes (and particularly those governing the behaviour of the singular elements, for which the purification cycles are usually designed) ;
- . absolute control of the operating points, through intensive automation : this requires the availability and integration of reliable, accurate operating models, as well as in-line analytical instruments ;
- . or instead, the development of an alternative extractant to tributylphosphate, endowed with better selectivity, but also offering all of T.B.P's advantageous and indeed indispensable qualities.

Note, incidentally, that many of these developments are also helpful in cutting plant operating costs, so that the advances procured are not merely limited to future industrial installations.

Increasingly compact equipment offers another avenue for cost reductions. The use of centrifugal contactors should help, and some special past achievements attest to this possibility. However, their generalization asks for better control of the kinetic aspects of the different steps in the process (owing to the shorter residence time that they imply), and the resolution of certain operating problems specific to them, or which are particularly acute in this type of unit (e.g. the presence of solid particles).

The reduction in the volume of wastes generated has already focused sustained efforts, and has led to significant breakthroughs. Paper [5] illustrates this aspect and presents the results obtained in this field at the UP3 plant at La Hague. Yet more room for progress remains. Besides the contribution clearly made by the measures listed above, this essentially resides in the trend towards a salt-free process and, perhaps to a lesser degree, in the search for an incinerable substitute for T.B.P.

The development of a salt-free process is aimed at the efficient management of process liquid wastes by allowing the unrestricted routing of the aqueous process effluents to the high level ones, thus achieving greater "concentration". The essential effort required in the extraction cycles concerns the search for alternatives to the alkaline sodium reagents used for solvent regeneration (stripping of cations and organic degradation products), also the generalization of electrochemical techniques to perform the different valency adjustment operations in the process (essentially plutonium, but other actinides and fission products potentially concerned).

The search for a solvent with features similar to those of tributylphosphate, but suitable for incineration, is also aimed to continue the effort to achieve more efficient waste management : the purpose is the elimination of what represents today a reduced, or even marginal if subjected to distillation, but inevitable waste in the present Purex process, due to the presence of phosphorus in the extractant molecule. Research has been conducted in France in this area, and molecules like N,N-dialkylamides [6] appear to yield highly encouraging results. Investigations must be intensified in various directions before deciding on the viability of such a substitution.

4°/ Yet one of the development guidelines emerging today as one of the most important for the Purex process is that of separations complementary to those that it achieves in the present stage. In some cases, these complementary separations could be designed to recover some valuable materials contained in the high-level effluents (platinoid elements, ...). But, in most cases, as with the Japanese OMEGA project and the French SPIN programme, the basic aim is to separate, as indicated in figure 1, from among the fission products, some elements exhibiting particular radio-toxicity and accordingly meriting specific treatment or conditioning (nuclear transmutation of long-lived radionuclides, for example).

Research has been under way for several years in the field of actinide partitioning. The TRUEX process (TRansUranian EXtraction) developed in USA and based on the chemical properties of CMPO (carbamoyl methylene phosphine oxide) is one of the most famous illustrations, and research is continuing today in an attempt to improve, adapt and optimize such well-established concepts, or to develop new ones. Thus, studies have been initiated in France in connection with the SPIN programme to develop an extraction process for minor actinides by an incinerable extractant. One of the most advanced concept is the DIAMEX process, the status of which is reported in this Conference [7]. The research supported by such programmes concerns :

- . basic research to identify and to optimize the appropriate extractant (or extractants, in so far as, beyond the initial extraction, there is a need for complementary purification operations, such as actinide/lanthanide separation downstream from the DIAMEX process) ;
- . process development studies (to solve all the chemical and radiolytic problems, especially those raised by the presence of certain fission products) ;
- . equipment engineering : the technologies considered may be different from those selected for the "core" of the process, in so far as the respective weight of the different criteria to be considered could be modified (capacity, cost and radiolytic stability of extractants). However, one of the major criteria will always be the ability to perform separations that generate a minimum amount of wastes, and the conventional liquid-liquid extraction techniques still appear to enjoy an advantage over some alternative concepts, promoting inorganic solid supports for example.

## CONCLUSION

The recovery and purification by the Purex process of the main valuable elements present in the irradiated fuel is an industrial reality today, as well as an undeniable technical success. The know-how accumulated, through the major R&D effort conducted, and from industrial experience, make it a mature process ; but further development efforts are still needed :

- . to confirm mastery of the process by generalized modelling (meeting both the needs of present operators and future designers) ;
- . to adapt the process to changes in the fuels to be reprocessed (actinide content, including  $^{238}\text{Pu}$ , as well as fission products, expected to increase) ;
- . to reinforce or perpetuate its competitiveness in economic terms (by optimizations or technical innovations) and with respect to the volume of waste generated ;
- . to perform complementary separations which appear advisable (in response to recovering objectives or to waste management concerns). These operations could initially be considered downstream from the core of the present process, but will probably ultimately have to fit into an integrated approach (direct single-cycle "complete" reprocessing ?).

While for the last objective mentioned, other separation processes may emerge and prove to be more effective in meeting the new separation objectives in the light of the criteria to be considered in this area (this is not a "*fait accompli*" today), it nevertheless remains true that mainly of the mentioned guidelines appear to be the unavoidable condition for the decades to come for deriving maximum benefit from industrial installations in operation today.

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Reactor class		GCR	LWR	FBR (precursor)
Fuel nature		U	UOX	UOX-PuOX
AVERAGE BURNUP (GWd.t <sup>-1</sup> )		4	33	80
F U E L  C O M P O S I T I O N  (g/t <sup>-1</sup> )	U	992500	955000	915000
	Pu	2600	9740	194000
	Np	22	433	180
	Am	-	325	2320
	Cm	-	23	80
	Zr	515	3580	6540
	Tc		814	2100
	Ru	200	2165	7240

TABLE 1 : EVOLUTION OF REPROCESSED FRENCH FUELS TYPICAL CHARACTERISTICS

NAME	DATE OF COMMISSIONNING	FUEL NATURE (Reactor class)	NOMINAL THROUGHPUT (tU/year)
UP1	1958	Metal (plutonigen reactors)	
UP2	1966	Metal (GCR)	400
UP2 HAO	1976	Oxide (LWR)	400
UP3	1989	Oxide (LWR)	800
UP2 800	(1994)	Oxide (LWR)	(800)

TABLE 2 : FRENCH REPROCESSING PLANTS MAIN FEATURES

AVERAGE BURNUP (GWd.t <sup>-1</sup> )		33	45	60
C O M P O S I T I O N (*)	Pu (% <sup>238</sup> Pu)	9740 (1,8)	11370 (2,9)	12990 (4,5)
	Np	433	611	887
	Am	325	530	765
	Cm	23	92	213
	Zr	3580	4730	6250
	Tc	814	1085	1403
(gt <sup>-1</sup> U)	Ru	2165	3068	4156

(\*) 3 years cooled

TABLE 3 : INCIDENCE OF AN INCREASED BURNUP OF LWR FUELS

PRODUCT	URANIUM			PLUTONIUM	
	Ruthenium	Neptunium	Plutonium	Ruthenium	Neptunium
1st cycle actual DF (1)	# 10 <sup>4</sup>	# 1	> 2.10 <sup>6</sup>	# 10 <sup>4</sup>	> 10
Specified global DF (2)	10 <sup>4</sup>	10 <sup>2</sup>	2.10 <sup>6</sup>	10 <sup>6</sup>	70
Extra DF needed	-	10 <sup>2</sup>	-	# 10 <sup>2</sup>	< 10

(1) from UP3 operating results

(2) UNIREP specifications

TABLE 4 : "SINGLE CYCLE" PROCESS TODAY'S REQUIREMENTS