

OVERVIEW OF THE LONG-LIVED RADIONUCLIDE SEPARATION PROCESSES DEVELOPED IN CONNECTION WITH THE CEA's SPIN PROGRAMME

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ABSTRACT :

One possible strategy for eliminating the long-term potential hazards associated with the storage of vitrified high level waste produced by the reprocessing of irradiated nuclear fuels, is the transmutation of the long-lived radionuclides in these wastes into short-lived radionuclides by nuclear means, which requires the prior chemical separation of these long-lived radionuclides from the nuclear waste mixture. To do this, the French CEA launched the SPIN (SÉPARATION-INCINÉRATION) research programme in 1991, under the law passed by the parliament on 30 december 1991.

Research currently under way to develop separation processes for some long-lived radionuclides concerns modifications of the PUREX process, and the development of new solvent extraction processes. The research directions are briefly summarized here.

PUREX process.

Modifications of the operating parameters of the PUREX process can certainly help to separate some long-lived radionuclides like ²³⁷Np and ⁹⁹Tc.

New processes :

Minor actinide separation processes. The strategy for these separations is based either on the extraction of the minor actinides from their stable oxidation states in aqueous nitric acid media (common in the reprocessing industry), or, especially for americium, after oxidation to high oxidation states. This research includes : ° *Minor actinide co-extraction using the DIAMEX process ; ° An(III)/Ln(III) separation ; ° Am selective separation after its oxidation to Am(IV) or Am(VI).*

Cesium extraction process using calixarenes extractants.

This lecture will focus on the latest developments in these research areas.

1. INTRODUCTION

Nuclear-generated electricity accounts for about 17 % of all the electricity produced worldwide. This industry is faced today with a problem of managing the wastes, which is considered acute by public opinion in the different nuclear countries and, in general, by world public opinion. Depending on national policy, these wastes consist either of irradiated fuels, in which case the energy materials (uranium and plutonium) are considered as wastes, or of the mixture of fission products, minor actinides and activation products resulting from the reprocessing of the fuels to recover the uranium and plutonium for recycling. To simplify and to lower the cost of the treatment and conditioning of spent fuel reprocessing wastes, and perhaps also to improve the public acceptance of nuclear power, considerable efforts have been mounted, with the aim of decreasing the unit volume of solid wastes (per ton of fuel reprocessed), particularly those intended for disposal in deep geological repositories. In this field, COGEMA has emerged as the prime mover of this strategy. At the reprocessing plants in La Hague, the unit volume of solid wastes generated in reprocessing operations, which justify deep geological disposal, is around 1.5 m³/t today, or about half of the volume initially defined in the process book. Following modifications to the PUREX process and the application of new processes, this unit volume is due to decrease drastically by the end of the century, when it should be around 0.465 m³/t [1]. The single distinguishing feature of nuclear waste management is their extreme danger, which, depending in particular on the nuclear properties of the radionuclides that they contain, may be spread over considerable periods of time. Faced with the growing opposition of public opinion to very long-term radwaste disposal techniques and the difficulty of the scientists to predict the behavior of the geological barriers for periods exceeding one hundred thousand or even one million years, it has become necessary to study and propose some technical solutions to this problem.

The separation and incineration of long-lived radionuclides by nuclear means, which lies at the source of the problem, in order to convert them to short-lived radionuclides, exhibiting higher activity, but which can feasibly be stored over a short period of time, is considered one possible solution to the problem. The situation is regarded with extreme caution in France, where more than 75 % of the electricity consumed is nuclear-generated. A law was accordingly passed by the French Parliament on 30 December 1991, ordering research to be conducted over a fifteen-year period, aimed in particular to determine the experimental conditions for the conversion of certain long-lived radionuclides present in the nuclear fuels to short-lived radionuclides by nuclear means. In this connection, the CEA launched the SPIN (SéParation/INcinération) program for the definition of long-lived radionuclide separation processes and for their destruction, chiefly by fast-neutron reactors [2]. This "intensive reprocessing" strategy is also being investigated in Japan, which launched the OMEGA program in 1988 [3], with objectives similar to those of the SPIN program.

This paper describes the main research guidelines selected at the CEA, aimed at the separation of long-lived radionuclides, and the latest experimental results obtained are briefly described.

2. PROBLEM ANALYSIS AND RESEARCH OBJECTIVES

The high-level wastes generated by irradiated fuel reprocessing, and intended for disposal in deep geological repositories, today include short- and long-lived radionuclides belonging to the families of fission products, minor actinides and activation products. It is universally acknowledged that the half-life identifying the borderline between short- and long-lived radionuclides is thirty years (half-life of ^{137}Cs). In fact, it is considered possible to develop safe disposal methods for periods of up to three centuries, or ten times the "borderline" period, the time necessary for the "total" decay of the short-lived radionuclides. After three centuries, the radionuclides which subsist in the stored wastes, particularly in the most active among them (nuclear glasses) will be the long-lived radionuclides. For the UOx reference fuel, irradiated to a burnup of 33 GWd/t and cooled for three years, Table 1 lists the long-lived radionuclides present, their abundance and some of their nuclear and radiotoxicological properties [4].

A glance at the data in Table 1 shows that the potential hazard of long-lived radionuclides is chiefly due to the minor actinides, and particularly the americium isotopes. This situation prevails for several tens of thousands of years. Consequently, efforts to develop separation methods will mainly concern the minor actinides, and especially americium. However, another way to tackle the problem is to consider the residual toxicity at the outlet of the geological formations where the nuclear wastes may be stored. This is currently being examined, particularly as part of the European exercise called PAGIS [5]. In this case, the doses delivered to the population in the neighborhood of the disposal site, although considerably lower than the standards currently in force, are mainly due to certain fission products, whose migration rates, with the water vector in the subsoil, are much greater than those of actinides. In consequence, a part of the research efforts is also focused on the separation of certain fission products, particularly technetium and cesium. Since long-lived radionuclides were also certainly not completely destroyed during a nuclear incineration cycle, it is also essential to guarantee the "reprocessability" of the targets or nuclear fuels which will contain these materials.

Table 1. Main characteristics of the long-lived radionuclides present in an irradiated fuel (UO_x type fuel ; burn-up : 33 GWd/t ; cooling time : 3 years)

Radio-nuclide	t½ (years)	Abundance (g/t _{H.M.})	Specific activity (Bq/g)	Dose factor for ingestion (Sv/Bq)	Isotopic %	Total element (g/t _{H.M.})
Fission products						
¹⁴ C	5.7 10 ³	0.13	1.05 10 ¹¹	5.7 10 ⁻¹⁰	100	0.13
⁷⁹ Se	6.5 10 ⁴	4.7	2.58 10 ⁹	2.3 10 ⁻⁹	8.6	54.6
⁹³ Zr	1.5 10 ⁶	714	9.3 10 ⁷	4.2 10 ⁻¹⁰	20.5	3617
⁹⁹ Tc	2.1 10 ⁵	814	6.3 10 ⁸	3.4 10 ⁻¹⁰	100	814
¹⁰⁷ Pd	6.5 10 ⁶	200	1.9 10 ⁷	3.7 10 ⁻¹¹	16.1	1240
¹²⁶ Sn	1.0 10 ⁵	20.3	1.0 10 ⁹	5.1 10 ⁻⁹	39.8	51
¹²⁹ I	1.6 10 ⁷	169	6.5 10 ⁶	2.4 10 ⁻⁸	81.2	208
¹³⁵ Cs	2.3 10 ⁶	1312	4.2 10 ⁷	1.9 10 ⁻⁹	37.2	3521
Minor actinides						
²³⁷ Np	2.1 10 ⁶	434	2.6 10 ⁷	1.0 10 ⁻⁶	100	434
²⁴¹ Am	4.3 10 ²	217	1.3 10 ¹¹	1.2 10 ⁻⁶	66.8	325
²⁴³ Am	7.4 10 ³	102	7.4 10 ⁹	1.2 10 ⁻⁶	31.4	325
²⁴⁵ Cm	8.5 10 ³	1.2	6.3 10 ⁹	1.2 10 ⁻⁶	4.7	25.5
Activation products						
⁵⁹ Ni	7.5 10 ⁴	36.1	3.0 10 ⁹	5.4 10 ⁻¹¹	--	36.1
⁶³ Ni	1.0 10 ²	6.6	2.1 10 ¹²	1.5 10 ⁻¹⁰	--	6.6
⁹⁴ Nb	2.0 10 ⁴	4	6.9 10 ⁹	1.4 10 ⁻⁹	--	4

The objectives of separative chemistry research connected with the SPIN program are listed in Table 2.

Table 2. Research objectives in separation processes [6]

Nature of the objectives	Importance
° Am separation (99 %)	Very important
° Ability for reprocessing	
° MO _x (LWR, FNR)	Very important
° Am targets (FNR ?)	Very important
° Cm, Pu, Np separation (99 %)	Important
° Ability for reprocessing	
° Fuels with Np (FNR ?)	Important
° Cm targets (FNR ?)	Important
° Long-lived F.P. separation	Secondary

3. SEPARATION OF LONG-LIVED RADIONUCLIDES

3.1. Strategy

Before presenting the strategic guidelines concerning the separative methods to be developed for some of the long-lived radionuclides mentioned above, it is essential to review the behavior of these materials in current nuclear fuel reprocessing operations. Table 3 presents this information for the specific case of COGEMA's UP3 plant at La Hague.

Table 3. Behavior of some long-lived radionuclides at COGEMA's UP3 plant at La Hague [4]

Long-lived radionuclide	Behavior
Minor actinides	
^{237}Np	<ul style="list-style-type: none"> ◦ 70 to 90 % extracted in the first U+Pu co-extraction cycle ◦ Np extracted separated in second U cycle ◦ All the Np is finally mixed with FP
$^{241, 243}\text{Am}$ ^{245}Cm	<ul style="list-style-type: none"> ◦ Not extracted, remains with FP
$^{239 \text{ to } 242}\text{Pu}$	<ul style="list-style-type: none"> ◦ 0.12 % of losses with wastes
Fission products	
^{99}Tc	<ul style="list-style-type: none"> ◦ ≈ 30 % of Tc is insoluble in fuel dissolution ◦ Soluble Tc is co-extracted with Zr(IV) and then Pu(IV) (and U(VI)) in the first U+Pu co-extraction cycle, and then separated by special washing and mixing with FP
^{135}Cs	<ul style="list-style-type: none"> ◦ Not extracted, remains with FP

In consequence, the separation strategies adopted are divided into two categories.

* Definition of operating conditions of the PUREX process (in the broad sense of the term) for the separation of some long-lived radionuclides. This strategy concerns ^{237}Np and ^{99}Tc . It could also be applied to ^{93}Zr and ^{129}I .

* Definition of specific separation processes. This concerns $^{241, 243}\text{Am}$, ^{245}Cm and ^{135}Cs .

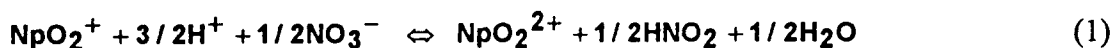
Due to its outstanding ability to solve separation problems in the nuclear industry, all the processes investigated are based on liquid/liquid extraction. For the difficult separation of americium and curium, the process being investigated has several cycles involving different extractants, whereas cesium can be separated using a single extractant.

3.2. Separation of long-lived radionuclides using the PUREX process

²³⁷Np

As stated above, most of the neptunium is extracted in the first U+Pu co-extraction cycle (1CUPu) applied at the UP3 plant in La Hague, and this fraction of extracted neptunium is mainly separated in the second uranium purification cycle (2CU). Hence the current research objective is to determine the physicochemical conditions of the PUREX process required to boost the neptunium extraction yield in 1CUPu. Two types of study are undertaken in this program : consolidation of the PAREX code used to predict the behavior of neptunium in the different steps of the PUREX process, and especially in the 1CUPu and 2CU cycles, and experimental investigations, in the laboratory, aimed to consolidate the knowledge of the redox reactions between the Np(V)/Np(VI) and HNO₂/HNO₃ pairs, and, in a test loop, to qualify the PAREX code for the behavior of neptunium. One may well ask why new studies appear necessary for the new objective, whereas the behavior of neptunium in the PUREX process has been investigated for many years. The answer is that the objectives previously assigned were chiefly aimed to prevent the uranium and plutonium end products from being polluted by neptunium, so that only an "overall" knowledge of neptunium behavior was then necessary, whereas the new objective implies a much closer understanding of this behavior.

The equation of the basic reaction allowing a "rough" interpretation of neptunium behavior in 1CUPu is the oxidation of Np(V) to Np(VI) by nitric acid, a reversible reaction catalysed by nitrous acid produced by reaction.



This reaction, which has been investigated for many years by Siddall and Dukes [7], Swanson [8] and Moulin [9], does not yet appear to have revealed all its aspects. One unanswered question is its kinetics in the presence of highly concentrated uranyl nitrate and of the solvent.

Valid methods nevertheless appear to be developing : increasing the temperature and the nitric acidity during extraction in 1CUPu should help to achieve the objective of quantitative neptunium extraction in 1CUPu without requiring the addition of a special reagent to oxidize the Np(V). This also represents the analysis of Yamana [10].

⁹⁹Tc

The behavior of technetium present in the fuel dissolution liquor (which accounts for about two-thirds of the Tc inventory of irradiated fuel) is unusual (in comparison with the other metallic species) during the operations of the PUREX process. The technetium exists in solution in oxidation state VII, in the form of the TcO₄⁻ ion. In this form, Tc(VII) is co-extracted with Zr(IV) (Tc(VII) playing an identical role to that of the nitrate anions), and then with Pu(IV) and U(VI) after washing of the Zr(IV) contained in the solvent. It is then possible to transfer Tc(VII) to the aqueous phase by washing with concentrated nitric acid (NO₃⁻/TcO₄⁻ competition effect) [11]. The behavior of the soluble fraction of Tc can therefore be considered to be under control. In consequence, research must focus on the understanding of the behavior of Tc in the irradiated fuel dissolution step, in order to identify simple methods that can be used to make the solubilization of the Tc quantitative. Investigations currently under way are designed to determine the precise metabolism of the Tc in the overall PUREX process which is a problem due to analytical difficulties, and to improve the Tc dissolution yield from the dissolution residues.

3.3. Separation of long-lived radionuclides with new processes

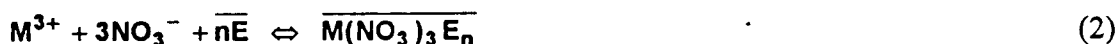
3.3.1. Minor actinides

Assuming the implementation of an "intensive reprocessing" strategy, the high-level raffinate leaving the "modified" ICUPu(Np) will only contain, as actinides, in addition to traces of uranium, neptunium and plutonium, the entire fuel inventory of americium and curium. The CEA is investigating two types of process to extract and separate these minor actinides from the FP : the first is based on the extraction of the actinides in their stable oxidation state in nitric medium, i.e. An(III), and the second process is mainly concerned with the separation of americium, and is based on its selective oxidation to Am(IV) or Am(VI) in the presence of a heteropolytungstate ligand, followed by selective extraction (SESAME process).

A common feature of these two processes is that, if they are applied directly to the raffinate from the PUREX process, after being subjected to a minimal modification of its composition. No decrease in the nitric acidity of the effluent is in fact intended, for preventing any risks of undesirable FP precipitation. In the first process, it is necessary to use several extraction cycles to achieve the objectives : first co-extraction cycle of minor actinides by the DIAMEX process (DIAMide EXtraction), applied to the raffinate from the PUREX process. In this step, the lanthanides (Ln(III)), which account for about one-third of all the FP, are co-extracted, and the mixture of An(III) + Ln(III) is obtained, free of strongly hydrolysable ions, such as traces of Pu(IV) and U(VI). The second An(III)/Ln(III) separation cycle uses an extractant with a nitrogen donor atom, such as the alkyl derivatives of tripyridinetriazine or picolinamides, allowing their separation by selective extraction of An(III) the least abundant metallic entities, so that only a minimal extraction capacity is required from the solvent. The third Am/Cm separation cycle could be applied either by the DIAMEX process or by the SESAME process. Note also that, for the first process, all the reagents to be employed (extractants, diluents, chelant reagents present in aqueous solution) will display the feature of being totally incinerable into gases releasable into the environment, thus helping to eliminate any generation of secondary solid waste. Consequently, these reagents will consist exclusively of C, H, N and O atoms.

DIAMEX

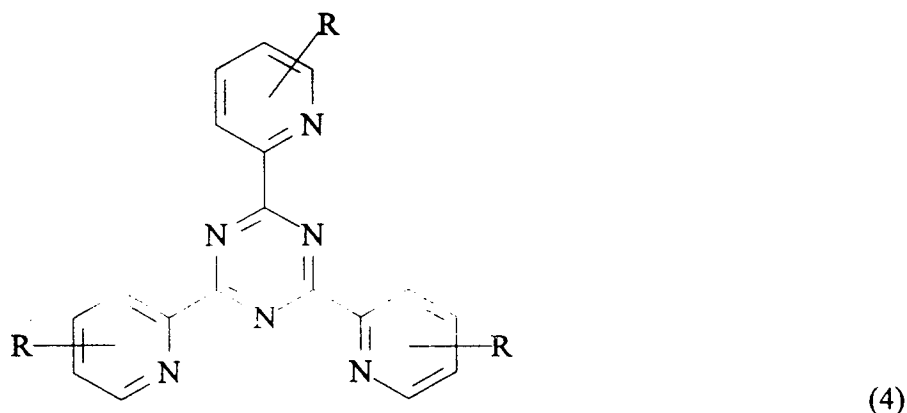
The extraction of the An(III) (Am and Cm) from the high-level raffinate produced by the PUREX process is difficult because of the low extraction capacity of the An(III) nitrates and by the high concentration of nitric acid, which induces strong competition in the extraction of the An(III) nitrates. The diamide extractants, proposed by Musikas [12], and particularly those belonging to the sub-class of malonamides, which have a single carbon that forms a bridge between the two amide groups, offer a solution to this problem of extraction. With the general formula $(RR'NCO)_2CHR''$, where R, R' and R'' are alkyl or oxyalkyl radicals, these compounds are bidentate oxygen donors, forming an extremely stable six-link ring with the metallic ion. The extraction mechanism essentially concerns the extraction of neutral molecules, and corresponds to the following equation :



where E is the diamide extractant (the species present in organic phase are overlined).

The value of n, the number of diamide molecules solvating the An(III) nitrate, is two at saturation of the organic phase. However, using the conventional slope method, the value of n found exceeds two, reflecting the non-ideality of the organic solutions of diamide, an occurrence often encountered in the extractive chemistry of the amides.

The first is based on the use of derivatives of tripyridinetriazine R_3 TPTZ [14], answering to the following semi-developed formula :

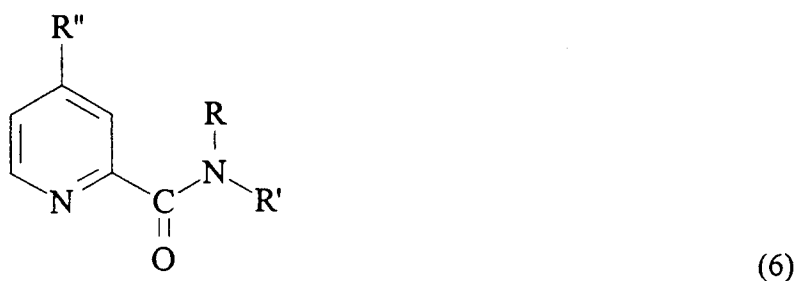


To be effective, the extractant R_3 TPTZ must be employed in synergistic combination with an HA acid extractant, a source of more lipophilic anions than nitrate ions. The extraction equation is then written :



The current research direction, pursued jointly with the team of Dr. M.J.Hudson of the University of Reading (UK), concern the synthesis of alkyl derivatives of TPTZ that are sufficiently hydrophobic and the synthesis of HA acids with low pK_a .

The second system concerns the use of picolinamide extractants, answering to the following general semi-developed formula :



As demonstrated by Cordier [15], pyridine 2 carboxamide, for which R, R' and R'' = H, a soluble reagent in the aqueous phase, is a selective chelatant of Am(III) with respect to Nd(III). The grafting of alkyl groups, R, R' and R'', helps to reinforce the lipophilic properties of the molecules and accordingly to enhance their ability as selective extractant for An(III).

The extraction equation is written :



Current research directions in this area are aimed to strengthen the affinity of picolinamides for An(III) nitrates, particularly in order to counteract the strong competition due to the extraction of nitric acid.

SESAME (Selective Extracting Separation of Americium by Means of Electrolysis)

Another alternative to separate americium, either directly from the raffinate produced by the PUREX process, or from the An(III)/Ln(III) mixture produced by the DIAMEX process, or even from the Am(III)+Cm(III) mixture, consists of its selective oxidation to Am(IV) or Am(VI) followed by its extraction. The chief difficulty to be overcome in this connection is the oxidation of Am(III) in nitric medium with acidity greater than 1 mol/l. In the case of the Am(III)/Am(IV) pair, in fact, this impossibility is thermodynamic (E_0 Am(III)/Am(IV) = 2.6 V/NHE), whereas it is rather kinetic in the case of the Am(III)/Am(VI) pair. By contrast, it is possible to oxidize Am(III) by chemical or by electrochemical means, subject to the presence in aqueous solution of a powerful ligand belonging to the heteropolytungstate family. For example, the ligand $P_2W_{17}O_{61}^{10-}$ is extremely effective for this purpose. Present in a concentration higher than of Am(III), it allows the oxidation of the americium to Am(IV), whereas for molar ratios lower than 1, the americium is oxidized to Am(VI). Other heteropolytungstate ligands are also satisfactory, such as silicotungstates. After oxidation, the americium can be extracted, either by amine salts in the case of Am(IV), or by bis-2,6 dimethyl-4 heptyl phosphoric acid for Am(VI). In these conditions, neither the lanthanides (except for cerium) nor the curium is oxidized, and is therefore easily separated from the americium. This is the basis of the SESAME process [16].

Active tests of the SESAME process are currently under way at Fontenay-aux-Roses, on raffinates from the PUREX process, and on an An(III)/Ln(III) mixture generated in 1993 during active tests of the DIAMEX process.

3.3.2. Fission products

Among the long-lived fission products that need to be separated, only ^{135}Cs is now the subject of intensive study at the Cadarache Nuclear Center, for the definition of a separation process. The extractant molecule expected to permit the separation of Cs(I), either from a 1 mol/l nitric acid solution, concentrated with sodium nitrate (4 mol/l), like the solution generated by evaporation processes for radioactive effluents, or a high-level raffinate produced by the application of the PUREX process, has been selected in the family of calixarenes. These molecules, in the form of a calix (hence their name) are pre-organized structures which, by the grafting of adequate functional groups, either on the upper rim or on the lower rim of the structure, help to define specific chelating sites for ionic species considered as targets. The use of these substituents also makes it possible to impart hydrophilic or lipophilic properties to the molecules, thus enabling them to act as chelating agents or extractants. The research project, conducted jointly with several European universities under a contract with the CEC, consisted of a screening of the different synthesized calixarenes for their aptitude for Cs(I)/Na(I) separation followed by the extraction of Cs(I) from nitric solutions. Spectacular performance was observed in these two areas with the following calixarenes : mono-ring calix[4]arenes and bis-ring-n calix[4]arenes. Very high separation factors $SF_{\text{Cs/Na}}$ close to $4 \cdot 10^4$ were obtained with certain molecules [17]. These molecules lend themselves well to extraction in the form of supported liquid membranes (SLM), which therefore help to perform separations with a very small quantity of extractant.

Research under way at Cadarache in this area is concerned with :

- * the demonstration of the feasibility of the extraction of ^{135}Cs (in a mixture with the other cesium nuclides) from a high-level effluent produced by the PUREX process,
- * the search for specific calixarenes for the minor actinides, allowing selective separation of An(III)/Ln(III).

4. CONCLUSIONS

Studies under way at the CEA in connection with the SPIN program aimed at the separation of long-lived radionuclides for their subsequent nuclear "incineration" (P & T strategy) have yielded promising results, both in the areas of the DIAMEX and SESAME processes, and in the selective separation of cesium. Yet the road is a long one before the definition of the flow diagrams of a facility that would implement these intensive reprocessing technologies. While it is possible to reasonably predict the feasibility of a process such as DIAMEX, this cannot be said of An(III)/Ln(III) separations, which are certainly more difficult to achieve, or of the SESAME and "calixarene" processes, which are still in the basic research or early development stage. It also appears clear that economic considerations will have to be taken into account when the process decisions are made. For the time being, criteria of simplicity and reliability will certainly prevail in these decisions. While it is possible to predict that the chemists will find solutions to these complex problems of long-lived radionuclide separation, it is also clear that considerable efforts will have to be made to develop industrially-viable solutions.

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