

STUDIES ON BEHAVIOUR OF SELENIUM AND ZIRCONIUM IN PUREX PROCESS

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Abstract

The studies about the behaviour of ^{79}Se and ^{93}Zr allow identifying the PUREX process streams in which these radionuclides remain. In this way, in further investigations, other specific separation techniques could be applied in order to get targets pure enough for their possible transmutation. The studies showed that the extraction of Se decreases when the acidity of the aqueous phase increases from 0.5 M to 8.0 M, obtaining D values from $1.1\text{E-}2$ to $3.4\text{E-}4$ respectively and the uranium concentration has not influence in the Se extraction up to 130 g/L. In the case of Zr, its distribution coefficient value increases when the acidity of the medium increases from $1.96\text{E-}2$ to $3.84\text{E}0$ and 3.1 M to 8.0 M respectively, but the study about the influence of the uranium concentration in the Zr extraction showed that the Zr distribution coefficient decreases down to $1.0\text{E-}2$ when the organic phase is 100% saturated in uranium (130 g/L). Then it can be concluded that ^{79}Se and ^{93}Zr remain in the raffinate of the first step of PUREX process.

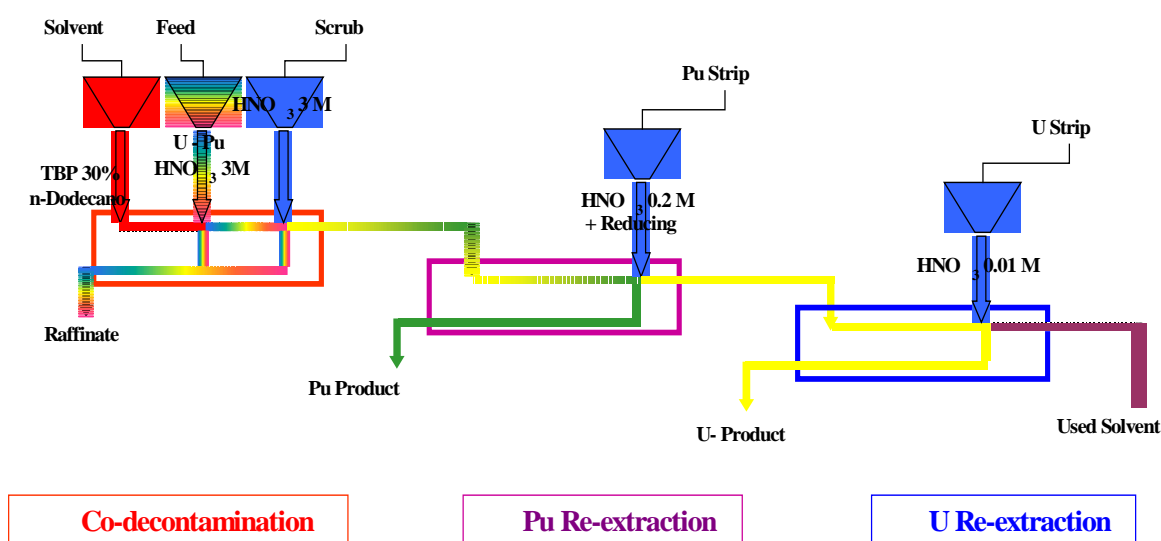
1. Introduction

The study of the behaviour of some fission products such as ^{79}Se , ^{93}Zr , ^{107}Pd and ^{126}Sn about their possible liquid-liquid extraction, together with uranium and plutonium, by the tributyl phosphate (TBP) in the main steps of the process for U and Pu separation and purification in the irradiated nuclear fuel reprocessing (PUREX process), is considered one of the main lines of the project *Long-lived Radionuclides Separation by Hydrometallurgical Processes* developed within the framework of CIEMAT-ENRESA agreement.

The main steps of the PUREX process consist on a jointly separation of U and Pu from the dissolution of a spent fuel (Figure 1), which are separated in a later step, by consecutive re-extraction processes, being necessary to reduce the oxidation state of Pu(IV) to Pu(III) and to use a weak acidic medium for U re-extraction. Then, both elements are purified independently by liquid-liquid extraction processes.

The aim of this paper is to show the studies carried out about the behaviour of ^{79}Se and ^{93}Zr , in order to identify the PUREX process streams in which these radionuclides remain. In this way, in further investigations, other specific separation techniques could be applied in order to get targets pure enough for their possible transmutation.

Figure 1. Simplified flow diagram of PUREX process



2. Experimental

2.1 Reagents

- Analytical grade TBP, n-dodecane, nitric acid, $\text{Na}_2\text{SeO}_3 \cdot 5\text{H}_2\text{O}$ and $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$.
- Uranium of nuclear purity prepared from nitric digestion of UO_3 .
- Beta-gamma tracers of ^{75}Se and ^{95}Zr (Amersham UK).

2.2 Chemical speciation

The oxidation states of selenium in nitric acid medium, considering the conditions in which the irradiated nuclear fuel is dissolved in the first step of PUREX process, can be (IV) and (VI), although Se(IV) is the most stable oxidation state in aqueous solution, and its chemical form in acid nitric medium is H_2SeO_3 [1].

The chemical form of zirconium is difficult to evaluate due to its strong tendency to hydrolyse. Depending on the medium acidity, zirconium forms complexes and generates a great variety of colloid species. The tetra-positive ion is considered the dominant zirconium specie in the first step of PUREX process, where the nitric acid concentration is high [2].

Depending on the acidity of the medium, zirconium can be extracted by TBP-dodecane in the form of di-, tri- or tetra nitrate complex [3-6]: $\text{Zr}(\text{OH})_2(\text{NO}_3)_2(\text{TBP})_2$, $\text{ZrOH}(\text{NO}_3)_3(\text{TBP})_2$, $\text{Zr}(\text{NO}_3)_4(\text{TBP})_2$.

2.3 Reference irradiated nuclear fuel

To calculate the concentration of Se and Zr present in an irradiated nuclear fuel, a burnt up of 40 000 MWd/tU, 3.5% enrichment and a cooling time of 5 years were considered. This reference fuel element is the same used by ENRESA in the calculation and assumptions concerning the project *Spent Fuel Characterisation and Behaviour under Relevant Repository Conditions* [7].

2.4 Experimental conditions and equilibrium diagrams

The studies were carried out considering a mass concentration of 67.5 g Se/tU and 4 284 g Zr/tU. The uranium concentrations considered were 25, 50, 100, 150, 200, 250 and 300 g/L.

Se(IV) and Zr(IV) equilibrium diagrams were obtained in the following conditions, which are those of the first extraction and scrubbing step of the PUREX process [8,9]:

- HNO_3 concentration: 3, 4 and 5 M.
- TBP in dodecane concentration: 20, 25 and 30% (v/v).
- Phase ratios (Or/Aq): 1, 2 and 3.
- Se(IV) concentration: 1.70, 3.40, 6.80, 10.2, 13.6, 17.0 and 20.4 mg/L
- Zr(IV) concentration: 0.11, 0.22, 0.43, 0.64, 0.86, 1.07 and 1.28 g/L.

The stable Se(IV) and the tracer ^{75}Se were prepared in the same chemical form SeO_3^{2-} . This specie was obtained by flow back boiling $\text{Na}_2\text{SeO}_3 \cdot 5\text{H}_2\text{O}$ and ^{75}Se in nitric acid 3, 4 and 5 M.

The stable Zr(IV) as ZrO_2Cl_2 and the tracer ^{95}Zr were treated successively with HNO_3 18 M to obtain the specie $\text{ZrO}_2(\text{NO}_3)_2$.

The influence of the uranium concentration was studied considering those nitric acid concentrations in which the extraction of both, Se(IV) and Zr(IV), was maximum. The uranium concentrations tested were ranged from 25 g/L to 300 g/L.

Plutonium was simulated with the non active chemically analogous element Ce(IV) being the total mass 2 861 gCe/tU.

Se(IV) and Zr(IV) were tested independently and the equilibria were carried out with TBP-dodecane as organic phase. The equilibria between nitric and TBP phases were reached by 30 minutes of mechanical shaking at 950 u/min and the separation was performed after 60 minutes of decantation time. ^{75}Se , ^{95}Zr , free $[\text{H}^+]$ and uranium determinations were carried out in both phases.

Results are detailed in Figures 2 to 7 and Tables 1 to 4.

2.5 Analytical procedures

- Determination of Se concentration: it is performed by gamma spectrometry using the net peak area at 136 keV line of ^{75}Se .
- Determination of Zr concentration: it is performed by gamma spectrometry using the net peak area at 724 keV line of ^{95}Zr .
- Determination of free $[\text{H}^+]$: the cations present in the sample are complexed or precipitated by an excess of oxalic/oxalate buffer at pH 7.0. The solution is potentiometric titrated with KOH 0.1 M until pH 7.0.
- Determination of U concentration (Method I): gravimetry as U_3O_8 .
- Determination of U concentration (Method II): it is performed by gamma spectrometry using the net peak area at 186 keV line of ^{235}U .

3. Results and discussion

3.1 Extraction of Se(IV)

The extraction equilibrium diagrams of Se(IV) show the typical isothermal curves that are generally obtained in these kind of studies (Figure 2). For all TBP concentrations studied, the extraction of Se(IV) decreases when the acidity of the aqueous phase increases. The maximum value of the distribution coefficient (D), obtained for the lower acid media in the steady state (1.83 M) is 4.5E-3 (Table 1), which indicates the low Se(IV) extraction in these conditions.

Figure 2. Isothermal equilibrium curves of Se(IV) with different HNO₃(M) and TBP-dodecane concentrations. Or/Aq phase ratio 1

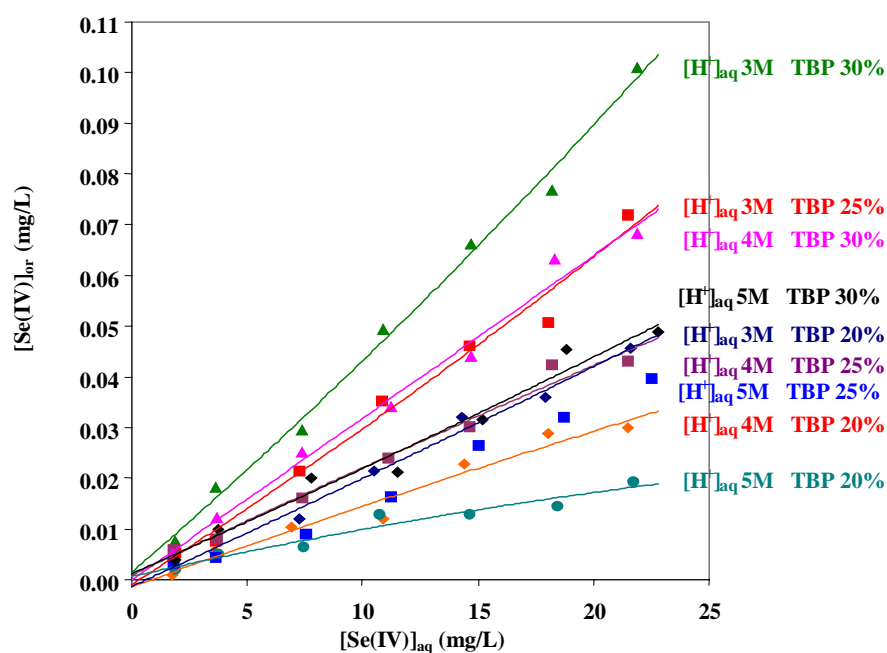


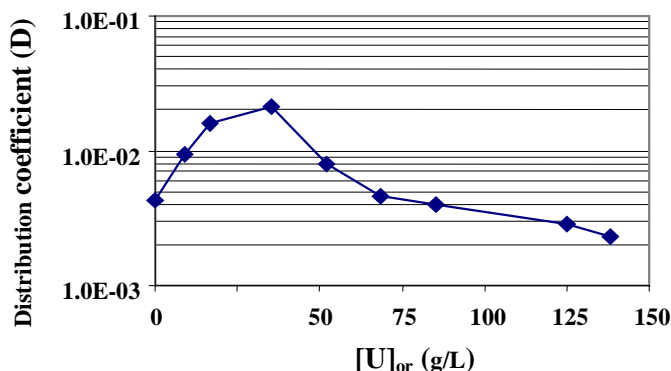
Table 1. Distribution coefficients of Se(IV) by TBP 30% in dodecane. Initial Se(IV) concentration 20.4 mg/L.

H ⁺ (M) Aq. phase	Ratio Or/Aq	Steady state					
		H ⁺ (M) Aq. phase	U (g/L) Aq. phase	U (g/L) Or.phase	Se(IV) (mg/L) Aq. phase	Se(IV) (mg/L) Or. phase	Distribution coefficient (D)
2.99	3	1.83	0	0	21.9	0.0977	4.46 E-3
2.99	2	2.12	0	0	22.0	0.0882	4.04 E-3
2.99	1	2.49	0	0	21.3	0.0733	3.44 E-3
3.90	3	2.53	0	0	21.9	0.0683	3.12 E-3
3.90	2	2.87	0	0	21.5	0.0563	2.62 E-3
5.27	3	3.43	0	0	22.8	0.0488	2.14 E-3
3.90	1	3.46	0	0	20.8	0.0450	2.16 E-3
5.27	2	3.90	0	0	22.0	0.0376	1.71 E-3
5.27	1	4.21	0	0	22.4	0.0296	1.32 E-3
3.02	3	1.93	< 0.5	9	21.9	0.204	9.32 E-3
3.00	3	1.92	1	17	21.6	0.348	1.61 E-2
2.94	3	2.00	1	36	21.5	0.453	2.11 E-2
3.14	3	2.24	1	52	22.4	0.178	7.96 E-3
3.03	3	2.30	2	68	22.8	0.105	4.60 E-3
3.07	3	2.47	6	83	23.4	0.0941	4.02 E-3
3.10	3	2.55	35	125	21.7	0.0621	2.86 E-3
3.09	3	2.60	170	138	22.2	0.0511	2.30 E-3

The influence of uranium and plutonium concentration in the distribution coefficient of Se(IV), was tested in the conditions in which the Se extraction is maximum (TBP 30% and HNO₃ 3 M).

The obtained results (Table 1 and Figure 3) show that uranium concentration has not influence in the extraction of Se(IV), because the D value increment is not significant. For this, it can be established that Se(IV) is not extracted in the first U and Pu co-extraction step of the PUREX process.

Figure 3. Influence of U concentration (g/L) on distribution coefficient of Se(IV), TBP-dodecano 30% HNO₃ 5 M



In order to complete the study about the influence of the aqueous nitric acid concentration in the Se(IV) extraction, samples with acid nitric concentrations between 0.5 M and 3 M and between 6 M and 8 M were analysed considering the maximum extraction conditions (TBP 30% and Se(IV) concentration 20.4 mg/L).

Figure 4. Influence of HNO₃ concentration (M) on extraction coefficient of Se(IV) by TBP-dodecane 30%

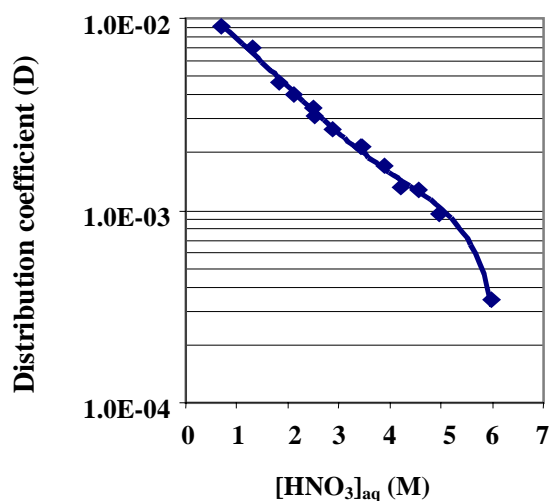


Table 2 and Figure 4 show that the tendency of the Se(IV) distribution coefficient is the same observed before, nevertheless the maximum D value obtained is 1.0E-2 that means Se(IV) is not extracted by TBP, so it can be concluded that ⁷⁹Se remains in the raffinate of the first step of PUREX process.

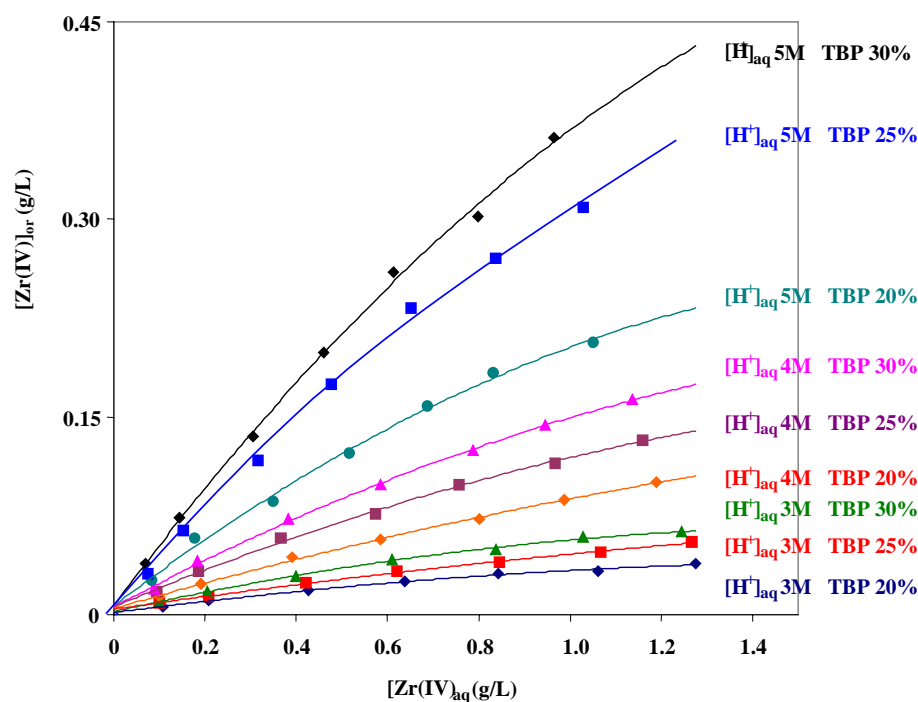
Table 2. Influence of aqueous acid nitric concentration less than 3 M and higher than 5 M, in the distribution coefficient of Se(IV) by TBP 30% in dodecane. Initial Se(IV) concentration 20.4 mg/L.

H ⁺ (M) Aq. phase	Ratio Or/Aq	Steady state			
		H ⁺ (M) Aq. phase	Se(IV) (mg/L) Aq. phase	Se(IV) (mg/L) Or. phase	Distribution coefficient (D)
0.524	3	0.39	21.0	0.223	1.06 E-2
1.06	3	0.69	20.9	0.191	9.12 E-3
2.13	3	1.31	21.4	0.149	6.98 E-3
6.17	3	4.56	22.3	0.0285	1.28 E-3
7.22	3	4.97	23.6	0.0228	9.67 E-4
8.20	3	5.99	22.9	0.0078	3.43 E-4

3.2 Extraction of Zr(IV)

The extraction equilibrium diagrams of Zr(IV) show the typical isothermal curves obtained in this kind of studies (Figure 5). Although the maximum extraction is obtained when the aqueous nitric acid and TBP concentrations are high, Zr(IV) is not extracted by TBP in a significant quantity because the maximum distribution coefficient value is 0.55 (Table 3) obtained for an acidity in the steady state of 4.7 M.

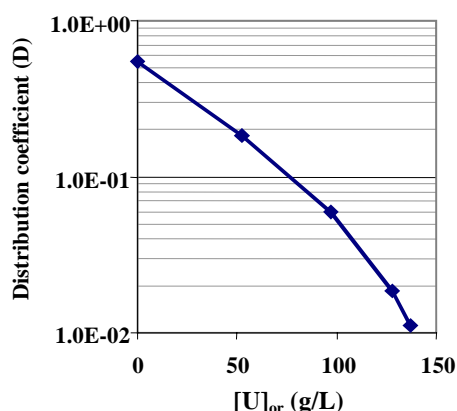
Figure 5. Isothermal equilibrium curves of Zr(IV) with different HNO₃ (M) concentration and TBP-dodecane % concentrations



The influence of uranium and plutonium concentration in the distribution coefficient of Zr(IV) was tested in the conditions in which the extraction is maximum, TBP 30% and HNO₃ 5 M.

The obtained results (Table 3 and Figure 6) show that when uranium concentration increases the Zr(IV) extraction decreases. The value of the distribution coefficient is very low (0.01) when the organic phase is 100% saturated with uranium (130 g/L). This effect shows that Zr(IV) is not extracted in the first cycle of co-extraction of U and Pu in the PUREX process.

Figure 6. Influence of U (g/L) concentration on distribution coefficient of Zr(IV), TBP-dodecane 30%, HNO₃ 5 M



Due to the extraction of Zr(IV) by TBP increases as the nitric acid concentration increases (Figure 5), it is necessary to study the behaviour of Zr(IV) when the nitric acid concentration, in the aqueous phase is higher (from 5 M to 8 M) than the range considered in the first studies and within the maximum extraction conditions TBP 30% and Zr(IV) concentration 1.28 g/L.

Table 3. Distribution coefficient of Zr(IV) by TBP 30% in dodecane. Initial Zr(IV) concentration 1.28 g/L

H ⁺ (M) Aq. phase	Ratio Or/Aq	Steady state					
		H ⁺ M Aq. phase	U g/L Aq. phase	U g/L Or. phase	Zr(IV) g/L Aq. phase	Zr(IV) g/L Or. phase	Distribution coefficient (D)
3.08	3	1.86	0	0	1.31	0.0256	0.0196
3.08	2	2.13	0	0	1.29	0.0395	0.0307
3.08	1	2.49	0	0	1.25	0.0626	0.0203
4.07	3	2.55	0	0	1.14	0.0580	0.0510
4.07	2	2.92	0	0	1.16	0.0951	0.0823
5.06	3	3.20	0	0	0.993	0.119	0.120
4.07	1	3.48	0	0	1.14	0.163	0.144
5.06	2	3.70	0	0	0.935	0.192	0.205
5.06	1	4.39	0	0	0.966	0.362	0.375
5.50	1	4.70	0	0	0.827	0.452	0.547
4.89	1	4.68	< 0.1	52	1.12	0.206	0.183
4.97	1	4.82	< 0.1	97	1.26	0.0762	0.0605
4.88	1	4.88	23	128	1.34	0.0248	0.0185
4.91	1	4.88	76	135	1.34	0.0159	0.0119
4.99	1	4.90	118	138	1.33	0.0150	0.0113
4.89	1	4.90	168	137	1.36	0.0140	0.0103

Figure 7. Influence of HNO₃ concentration (M) on distribution coefficient of Zr(IV) by TBP-dodecane 30%

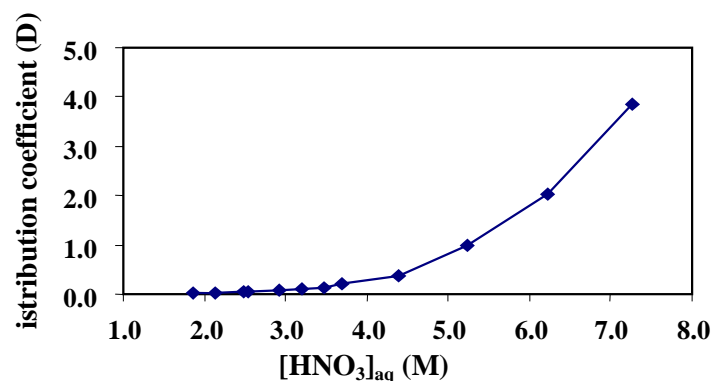


Table 4. Influence of nitric acid concentration higher than 5 M on the distribution coefficient of Zr(IV) by TBP 30% in dodecane. Initial Zr(IV) concentration 1.28 g/L.

H ⁺ (M) Aq. phase	Ratio Or/Aq	Steady state			
		H ⁺ (M) Aq. phase	Zr(IV) (g/L) Aq. phase	Zr(IV) (g/L) Or. phase	Distribution coefficient (D)
5.50	1	4.70	0.827	0.452	0.547
6.10	1	5.24	0.641	0.635	0.990
7.03	1	6.22	0.421	0.854	2.030
7.95	1	7.26	0.259	0.994	3.840

Results from Table 4 and Figure 7 show that the distribution coefficient values of Zr(IV) increase when the HNO₃ concentration increases, being the distribution coefficient higher than 1.0 for HNO₃ concentration higher than 6 M and close to 4.0 for acid concentrations of 8 M. This behaviour could be useful for a possible separation of ⁹³Zr from the raffinate of the first cycle of PUREX process, in which it has been demonstrated that Zr remains totally.

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