EURO-GANEX, a Process for the Co-separation of TRU

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Abstract

The EURO-GANEX process was developed to co-separate all transuranic (TRU) elements from used nuclear fuel without generating a pure plutonium product. A solvent consisting of TODGA + DMDOHEMA in kerosene co-extracts TRU together with the lanthanides. Co-extraction of Zr and Pd is suppressed by CDTA. A solution containing SO_3-Ph-BTP + AHA in HNO_3 is used to strip TRU from the organic phase. The remaining lanthanides are stripped by dilute HNO_3. Based on the results of a spiked test and some further flow sheet calculations a hot demonstration test was performed in a 16 + 16 stage centrifugal contactor rig. A genuine feed solution was prepared by dissolving irradiated fast reactor fuel and removing uranium by a GANEX 1st cycle process. The raffinate from this process, containing TRU and fission products, was adjusted to 10 g/L Pu and was used as feed for the EURO-GANEX process. The product solution of this process contained 99.9% of the TRU inventory and 0.06% of the lanthanide inventory.

Introduction

GANEX (grouped actinide extraction) processes simultaneously co-separating all transuranic (TRU) actinide elements (Np, Pu, Am, and Cm) are suitable for homogeneous recycling strategies. They show potential benefit regarding process simplification and proliferation resistance because there is no pure Pu stream throughout the process. After the separation of U from irradiated fuel in the 1st GANEX cycle, TRU are co-separated in the 2nd cycle. Both cycles have successfully been hot tested at the CEA.[1,2]

Recently, alternative 2nd cycle processes have been developed and tested as part of the European 7th Framework ACSEPT[3] project: the CHALMEX[4,5,6,7] process and the EURO-GANEX process. The basic principle of CHALMEX is similar to that of the 1cycle-SANEX process,[8,9,10] i.e. selective extraction of actinides only from the feed solution. EURO-GANEX resembles TALSPEAK[11,12] or i-SANEX processes,[13,14] i.e. co-extraction of actinides and lanthanides followed by selective back extraction of actinides.

EURO-GANEX system

A solvent able to extract > 10 g/L Pu together with the other TRU was developed,[15,16] consisting of 0.2 M *N,N,N',N'*-tetra-*n*-octyl-diglycolamide (TODGA) + 0.5 M *N,N'*-dimethyl-*N,N'*-dioctyl-2-(2-hexyloxyethyl)malonamide (DMDOHEMA) in a kerosene diluent (Exxsol D80), see Figure 1. This solvent co-extracts TRU, lanthanides, Zr and Pd.

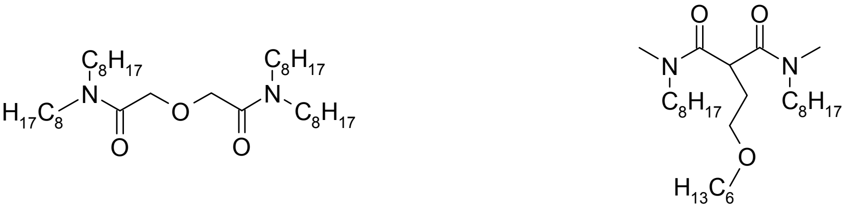

Figure 1. TODGA and DMDOHEMA, EURO-GANEX extracting agents.

1,2-Cyclohexanediaminetetraacetic acid (CDTA) was shown to suppress the extraction of Zr and Pd under the conditions relevant to the EURO-GANEX process.[17] The selective TRU back extraction from the solvent loaded with TRU + Ln was shown to be possible[17] using SO_3-Ph-BTP[18] + AHA (see Figure 2).[19]

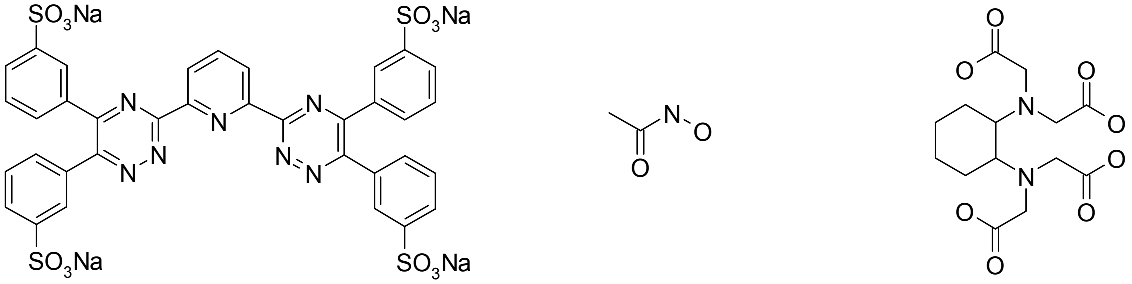

Figure 2. SO_3-Ph-BTP, AHA and CDTA, EURO-GANEX complexing agents.

A flow sheet for a EURO-GANEX process was developed and a successful spiked test was performed, using a feed solution containing 10 g/L Pu.[20]

A hot EURO-GANEX test was recently performed at JRC-ITU. Irradiated fast reactor fuel was oxidised and dissolved. U was selectively extracted from the dissolution solution by a GANEX 1st cycle process, similar to the one developed and tested by the CEA.[1] The raffinate from this process was used as feed solution for the EURO-GANEX process.

Fuel dissolution

116.8 g (with cladding) of ex-Dounreay fast reactor UC, UN or U(C,N) fuel pieces of less than 10 mm length were selected, thermally treated for oxidation and subsequently dissolved in 6 M HNO_3 to yield about 560 mL fuel solution as feed for the 1st GANEX cycle. The solution was characterised by ICP-MS measurements and titration for the acidity, see Table 1.

Table 1. Concentration of actinides and HNO_3 in the fuel dissolution solution and in the GANEX feed solutions.

	Fuel sol'n	1st cycle	2nd cycle
U	118 g/L	103 g/L	34 mg/L
Np	0.021 g/L	0.017 g/L	97 mg/L
Pu	24.8 g/L	22.7 g/L	10.1 g/L
Am	0.35 g/L	0.33 g/L	0.13 g/L
Acidity	4.0 M	5 M	5.9 M

GANEX 1st cycle

The GANEX 1st cycle is already well investigated and has been demonstrated on genuine fuel solution in the ATALANTE facility at CEA.[1] It is based on a selective uranium extraction by a monoamide (DEHiBA) dissolved in kerosene at an acidity of roughly 5 M. The problem elements are mainly Tc and Np which are reduced and scrubbed by hydrazine in a connected scrubbing section at 1.5 M HNO_3. Uranium is stripped at low acidity, 0.01 M.

A successful test in CEA was carried out in mixer settlers at a feed U and Pu concentration of 176 g/L and 2.5 g/L, respectively. Based on the experiences gained, a new flowsheet was designed, taking into account the much more Pu rich feed (Pu, 23 g/L; Table 1) as well as the shorter hold up times of the 16 stages centrifugal contactor system installed in the hot cell facility of ITU. Due to the limited number of centrifugal contactors it was decided to run the experiment in 2 steps, one step for extraction and scrubbing collecting the loaded organic phase. The second step is back extraction of uranium.

The U product solution contained 99.9 % of U, 3.1 % of Np, 0.1 % of Pu and 24.4 % of Tc; Am and Ln were not detected. The raffinate (to be used as feed for the 2nd cycle) contained 0.1% of U, 96.9 % of Np, 99.9 % of Pu, 100 % of Am and Ln and 75.6 % of Tc.

Essentially all uranium was removed and essentially all other actinides were routed to the raffinate. So whilst some optimisation of the GANEX 1st cycle can be made, the main goal of this experiment was demonstrated, i.e. removal of the large mass of uranium before the 2nd cycle GANEX. About 600 mL of feed solution to the 2nd GANEX process was produced, enough for a demonstration test.

GANEX 2nd cycle (EURO-GANEX) – hot demonstration test

The flow sheet used for the hot test is based on a flow sheet developed and tested in spiked centrifugal contactor trials at NNL.[20] Following modelling using the CEA PAREX code, some modifications were introduced in order to improve the control of key species across the flow sheet whilst adapting to the 16 stage set-up in ITU's hot cell facility. As 16 stages are not enough to cover the complete flow sheet it was decided to divide the demonstration test into two consecutive days, 16 stages for extraction and scrubbing and 16 stages for back extraction.

To prepare the feed solution, the raffinate from the 1st GANEX cycle was adjusted to 10 g/L Pu and the acidity increased to 5.9 M HNO_3 (Table 1). In addition, CDTA was added[21] to suppress extraction of problematic FP (Pd, Zr) and a small amount of Np was added to increase concentration and the ease of analysis. 12 extraction stages in combination with the higher acidity was chosen to optimise Np(V) disproportionation and efficiency of extraction.

Day 1 – Extraction and scrubbing

The day 1 flow sheet (extraction and scrubbing) is shown in Figure 3. The experiment was started up with a 5.9 M pure HNO_3 solution as feed solution, switching to the real feed only after stable conditions and good phase separation had been obtained. The experiment was run for 6 hours to build up steady state conditions and continued for another 10 hours for collection of loaded organic phase at steady state. After shutting down, around 300 mL of loaded organic phase had been produced, which was sufficient as feed for the second day An back extraction flow sheet.

Recoveries are shown in Figure 3. Using 12 extraction stages near complete separation of actinides was achieved. In particular, losses of Np to the raffinate were minimal (less than 0.1 %). This is a substantial improvement over the spiked test[20] (with 24% lost to the raffinate) — probably due to the radiation induced oxidation and faster disproportionation of Np(V).

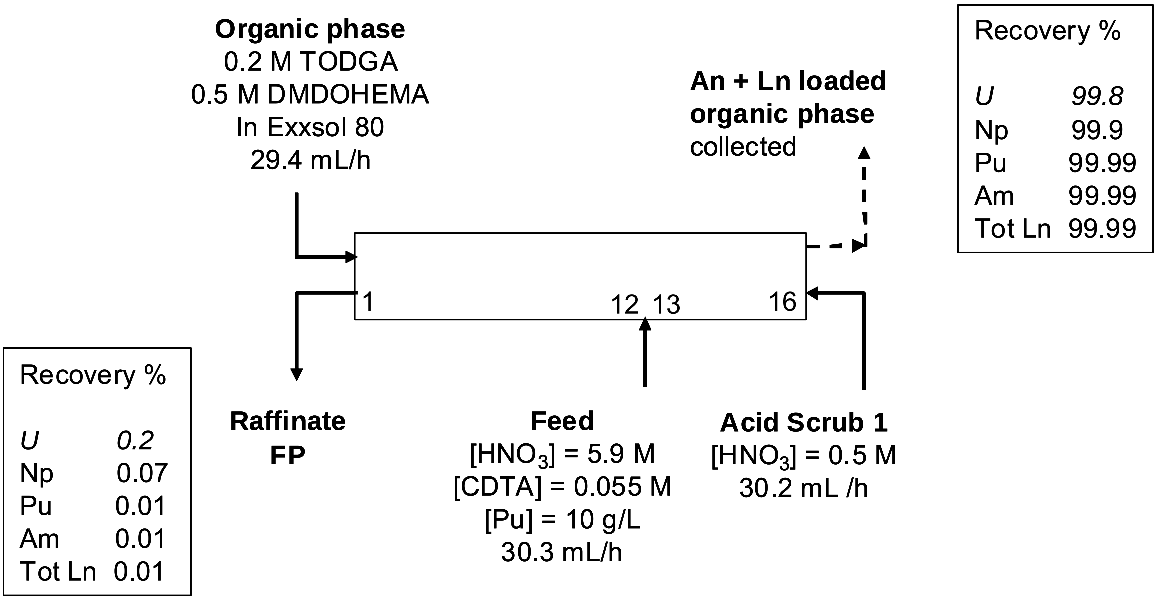

Figure 3. EURO-GANEX flow sheet – TRU extraction and scrubbing.

Day 2 – Back extraction

In order to minimise degradation by radiolysis of the loaded organic phase, the back extraction experiment was started as soon as possible after ending the extraction experiment. In practice, about one day (24 hours) was needed as preparation time. The flow sheet used for the back extraction of actinides and lanthanides is shown in Figure 4. Selective back extraction of actinides is achieved by a mixture of water soluble BTP in combination with AHA, at an acidity of 0.5 M in 6 stages. 6 stages are used for re-extraction of lanthanides back extracted with the actinides, using fresh organic phase. Finally 4 stages are used for back extraction of lanthanides using 0.01 M HNO_3.

The experiment was started up using the loaded organic solvent from the steady state build up phase of the previous extraction experiment. This was run for about 3 hours, before switching to the loaded organic solvent from the steady state collection. The experiment continued for approximately 4 hours which was enough to reach steady state conditions of the actinides.

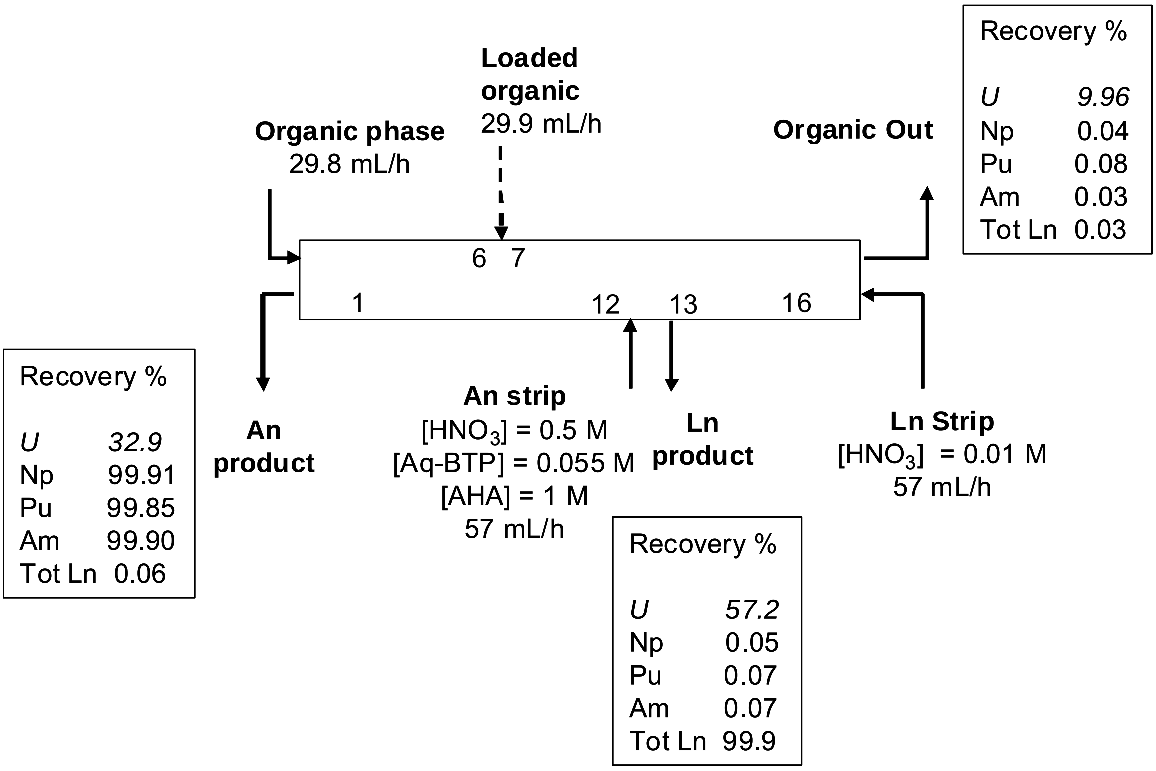

Figure 4. EURO-GANEX flow sheet – TRU back extraction.

Recoveries of actinides and lanthanides are listed in Figure 4. It is evident that the process has been highly successful. An almost complete recovery (99.9 %) of Pu, Np and Am has been achieved. The selectivity is also excellent with less than 0.1 % of the lanthanides in the actinide product. The lanthanides have also been efficiently back extracted into the Ln product (recovery > 99.9 %), together with less than 0.1 % of the actinides. The level of An and Ln impurities in the used solvent is also less than 0.1 %. Impurity levels can be managed to even lower levels if more stages are added. Note that the U results relate to the very small fraction of U present in the 2nd cycle feed solution (34 mg/L).

Conclusions

With these experiments a new GANEX 2nd cycle, the EURO-GANEX process, was successfully demonstrated, i.e. the global recovery of all actinides, using a Pu rich fast reactor fuel. This was one of the main objectives of the ACSEPT programme.

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