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Radiochemical reprocessing of V–Cr–Ti alloy and its feasibility study

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Abstract

An extraction scheme for radiochemical reprocessing of an activated vanadium–chromium–titanium alloy after a fusion reactor decommissioning was developed and checked experimentally. It is based on extraction of V, Cr and Ti freed of activation products from the alloy dissolved in nitric acid. The solution of di-2-ethyl-hexyl-phosphoric acid (D2EHPA) in a hydrocarbon solvent (dodecane) serves as an extractant. It takes 50 extraction steps to recover V, Cr and Ti down to an effective dose rate <12.5 μSv/h, permitting the refabrication of these metals without biological shielding from ionizing radiation. Technical and economic analysis suggests that the reprocessing alternative is more attractive economically than the burial of spent V–Cr–Ti alloy components.
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1. Introduction

A DEMO fusion reactor operates up to 35 MW year/m^2 fluence, which causes considerable activation of its structural materials. One of the candidate structural materials for the DEMO fusion reactor (that is, for the first wall, blanket and divertor) is the vanadium–chromium–titanium (V–Cr–Ti) alloy with the costly vanadium as the main component (up to 90 wt%) [1].

From this perspective, there is good reason to consider the possibility of the alloy regeneration and refabrication. However, to be able to safely handle a material as if it were non-radioactive, it is necessary to bring its effective dose rate (EDR) down to 12.5 μSv/h or less. In the case of the V–Cr–Ti alloy, a suitable method for achieving such a substantial radioactivity reduction is radiochemical reprocessing.

One practical outcome of our research is the basic diagram showing the principle of radiochemical reprocessing the V–Cr–Ti alloy for its subsequent refabrication. The diagram is shown in Fig. 1. The technological steps include the alloy dissolution in nitric acid [2] and reprocessing of the solution by extraction of V, Cr and Ti free of activation products [3–7]. The solution of di-2-ethyl-hexyl-phosphoric acid (D2EHPA) in a hydrocarbon solvent (dodecane) serves as an extractant.

In our extraction experiments, we used an unirradiated 90% V + 5% Ti + 5% Cr alloy. The experiments were carried out in static conditions with the goal of finding out how vanadium, chromium, titanium and radioactive isotopes are distributed between the aqueous and the organic phases. Radioactive isotopes ^{60}Co, ^{152}Eu, ^{110}Ag, ^{55}Fe and ^{99}Mo, which simulated the behavior of the activation products were introduced into the nitrate solution containing the dissolved alloy [4].

Based on the estimated element distribution factors in the extraction and reextraction processes, and

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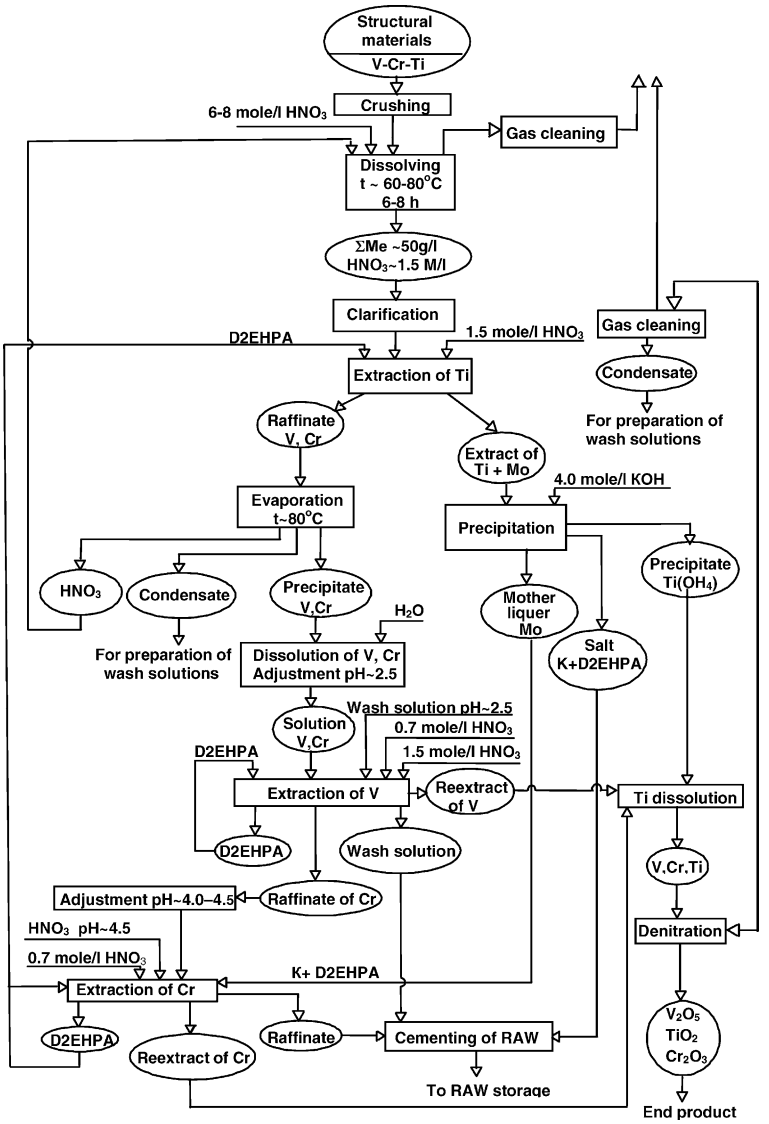

Fig. 1. Schematic diagram of V–Cr–Ti alloy radiochemical reprocessing.

computations, we found that it takes 48 extraction/re-extraction and purification steps to recover V, Cr and Ti with EDR below 12.5 μSv/h, permitting the refabrication of these metals without biological shielding. Eight of them are intended for Ti extraction/reextraction and purification, 26 – for V and 14 – for Cr.

Table 1 presents the expected degrees of the V–Cr–Ti alloy components purification, while Table 2 shows the required degree of purification for the V–Cr–Ti alloy (considered in Russian DEMO design [1]) that would permit hands-on refabrication [4]. A degree of alloy purification from a specific radioactive isotope or element here is a ratio of this isotope (or element) content in the alloy coming for reprocessing and in the alloy (or in its component) being end product.

Table 1
Expected degrees of V–Cr–Ti alloy component purification from activation products in extraction reprocessing

Component	^{99}Mo	^{60}Co	^{110}Ag	^{55}Fe	^{52}Eu
V	$\sim 10^2$	$>10^5$	$>10^5$	$>10^5$	2×10^3
Ti	$>10^5$	$>10^5$	$>10^3$	$>10^2$	$>2\times 10^2$
Cr	$>10^5$	$>10^5$	20	$>10^5$	$>10^5$

Table 2
Degrees of V–Cr–Ti alloy purification from specific impurities to permit hands-on refabrication [1]

Impurity element	Time after the reactor shut-down, years		
	10	20	30
Co	3×10^5	8×10^4	2×10^4
Ni	10^4	3×10^3	700
Fe	800	200	30
Eu	700	320	130
Sm	500	300	80
Nb	100	100	100
Mo	100	100	80
Cu	40	10	–
Tb	30	30	30
Ag	20	20	20

2. Extraction reprocessing

The reprocessing includes the following steps:

- Reception, interim storage and crushing or shearing of the structural parts made of the V–Cr–Ti alloy.
- Dissolution of the V–Cr–Ti alloy with 6–8 mol/l nitric acid solution at 60–80 °C for 6–8 h to give an overall metal concentration of ~50 g/l.
- Clarification of the obtained solution using percolating filters to remove undissolved particles.
- Extraction of titanium and molybdenum using 30% D2EHPA dissolved in paraffin. Titanium is recovered as a titanium hydroxide precipitate by reextraction performed statically using a 4.0 mol/l KOH solution, while Mo remains in the aqueous phase. Following the Ti and Mo separation, the extractant – a D2EHPA potassium salt – is delivered to the Cr-extraction unit. The aqueous mother liquor containing Mo is directed to the radioactive waste (RAW) cementing.
- Evaporation of the raffinate containing V and Cr. This involves segregation of the condensate and nitric acid fractions, which are used for the preparation of wash solutions and for the V–Cr–Ti alloy dissolution.
- Dissolution of the precipitate containing V, Cr and practically all the activation products followed by pH adjustment of the solution to about 2.5.
- Vanadium extraction using the D2EHPA solution. Vanadium, reextracted with a 0.7 mol/l nitric acid solution, is washed using a 'fresh' D2EHPA solution flow. The circulating extractant is regenerated with a 1.5 mol/l nitric acid solution. The wash solution used in this operation, which mainly contains rare earth elements and other V–Cr–Ti alloy activation products, is routed to the RAW cementation.
- Chromium extraction from the V-extraction cycle raffinate (with pH in the solution adjusted to ~4.0–4.5) using the D2EHPA potassium salt, previously employed in the Ti-extraction. The Cr-extract is rinsed using a wash solution with pH ~ 4.5. Chromium reextraction is performed with a 0.7 mol/l nitric acid solution. The raffinate containing activation products is sent to the RAW cementation.
- Dissolution of the titanium hydroxide precipitate using the V and Cr reextracts, and then obtaining marketable product, containing V, Cr and Ti oxides, by the method of plasmochemical denitration (or by another alternative technique). Condensate after the denitration is used for the preparation of wash solutions.
- Cementation of RAW, containing practically all the activation products separated during the V–Cr–Ti alloy radiochemical reprocessing, into cement blocks.
- Containerization of cemented RAW and transfer to long-term controlled storage.

3. Technical and economic analysis

The diagram in Fig. 1 suggests that the proposed radiochemical reprocessing is basically practical. However its economic attractiveness remained questionable. To evaluate this issue, a comparison had to be made between the activated V–Cr–Ti alloy reprocessing technology and the alternative burial concept. The burial process chart is represented in Fig. 2.

The two alternative technological solutions for handling the V–Cr–Ti alloy – processing versus burial – were compared economically. Computations were made on the assumption that the capacity of the processing

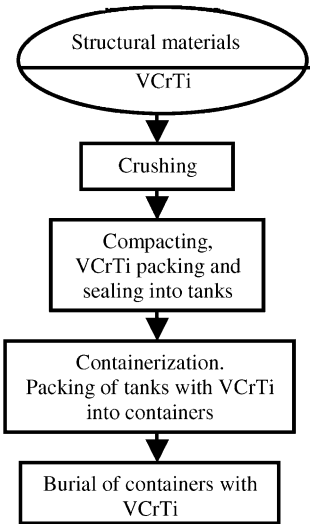

Fig. 2. Schematic diagram of a V–Cr–Ti alloy treatment using containerization and subsequent long-term storage of solid radioactive waste.

Table 3
Technical and economical characteristics of V–Cr–Ti-alloy radiochemical processing and container burial alternatives

Characteristic	Unit of measure	Alternative	
		Radiochemical reprocessing	Container burial
Mass of V–Cr–Ti alloy	t/year	400	400
End product (V_2O_5, Cr_2O_3, TiO_2)	t/year	380	–
Total investment of which constructing and	10^6 RUR	529	122
mounting work	10^6 RUR	178	61
Alloy handling service costs	10^6 RUR	102.6	37.6
Standardized profit (25%)	10^6 RUR/year	25.7	9.4
Cost of end product			
at US \$250/kg	10^6 RUR/year	3040	–
at US \$10.5/kg	10^6 RUR/year	128	–
Standardized profit plus cost of end product			
at US \$250/kg	10^6 RUR/year	3066	9.4
at US \$10.5/kg	10^6 RUR/year	153	9.4
Pay-back period at the cost of end product			
at US \$250/kg	years	0.2	13
at US \$10.5/kg	years	4	13

plant (or, in comparison, the flow of the alloy to the storage facility) would be 400 metric tons a year.

The economic feasibility of the alternative processes was assessed based on the estimated pay-back period, that is, the length of time necessary for the positive cash flows generated by the sales of products or services to recoup the initial investment. When assessed from this perspective, the solution with the lesser pay-back time is preferable. To determine the pay-back period, we preset a profitability level enabling a normal operating industrial and economic activity.

The commercial prices of vanadium (traded in the form of oxides) depend largely on the production scale and market demand, and can vary in a wide range. Also, much depends on product quality. According to [8], the price of V_2O_5 for 97% purity was US\$25/kg, while for 99.99% purity it was US\$4000/kg in 1998 prices. However, the information from different sources is inconsistent. For our purposes, we used two V_2O_5 prices \$250/kg and \$10.5/kg.

To assess the investment needs for the two alternative V–Cr–Ti alloy handling projects, we used data on analogues and aggregated values, as well as expert estimates, with allowance made for the construction-related costs.

It was assumed that all the radiochemical reprocessing operations would be performed in one building with a volume of 60 000 m^3. The cemented compound, loaded into safe 1 m^3 concrete containers, would be placed in an aboveground storage facility (24 000 m^3). The containers would arrive at the storage facility at a rate of 120 a year.

The no-processing alternative would require storing of the alloy in sealed 200 l tanks inside concrete containers accommodating four tanks each. Each year, the storage facility would receive 330 ferroconcrete containers. The construction volume of the facility would be 80 000 m^3.

Table 3 summarizes the technical and economic characteristics of the two V–Cr–Ti alloy handling alternatives. Metal extraction in the reprocessing operation was assumed to be ~95%. Conversion of US dollars into Russian rubles (RUR) was performed at the RF Central Bank's exchange rate as of the forth quarter of 2002 (US \$1 = 30 RUR).

These figures suggest that the reprocessing alternative is much more attractive economically than the burial of spent V–Cr–Ti alloy parts. Even at V_2O_5 price of \$10.5/kg, the initial investment in the radiochemical reprocessing project is returned in 4 years, while in the burial alternative, the pay-back time is 13 years – regardless of the V_2O_5 price.

However, this technical and economic evaluation is preliminary. The uncertainties precluding a more definitive assessment are the price of V_2O_5 and the fact that the proposed radiochemical reprocessing has only been tested in laboratory, under static extraction conditions and using modeling solutions.

4. Conclusions

(a) An extraction scheme for radiochemical reprocessing of an activated V–Cr–Ti alloy after a fusion reactor decommissioning was developed and checked experimentally. It is based on extraction of V, Cr and Ti freed of activation products from the alloy dissolved in nitric acid. The solution of

di-2-ethyl-hexyl-phosphoric acid (D2EHPA) in a hydrocarbon solvent (dodecane) serves as an extractant. It takes 48 extraction steps to recover V, Cr and Ti down to an effective dose rate <12.5 μSv/h, permitting the refabrication of these metals without biological shielding from ionizing radiation.

(b) Technical and economic analysis suggests that the reprocessing alternative is more attractive economically than the burial of spent V–Cr–Ti alloy components.

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