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Optimisation of inert matrix fuel concepts for americium transmutation

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Abstract

Concepts of inert-matrix fuels for americium transmutation are discussed. It is demonstrated that a 'hybrid' fuel design, consisting in a dispersion of an americium-bearing phase in an inert matrix, is desirable. More than a solid-solution is preferred in order to localise within a small volume the damage in the matrix due to fission fragments. Such a dispersion is composed of spherical inclusions (between 50 and 300 μm) of an americium host phase in a dense inert matrix. For an oxide fuel, we recommend the solid solution $(Zr,Am)O_2$, possibly stabilised by yttrium as the host phase. For a nitride fuel, $(Zr,Am)N$ is proposed. MgO and $MgAl_2O_4$ (oxide fuel), as well as TiN and ZrN (nitride fuel) are the most likely candidates for the inert matrix. Recommendations are also given for the research required to optimise the concept. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Americium contributes about 10% to the radiotoxic inventory in spent nuclear fuel. For a storage period of 250 to 100,000 yr, the remaining 90% are mainly due to plutonium. Therefore, transmutation of americium is being studied as a means to reduce the radiotoxic inventory of the high level waste arising from reprocessing. It is a technique that is complementary to plutonium recycling. In Europe, extensive research on americium transmutation is performed by the partners in the Experimental Feasibility of Targets for TRAnsmutation (EFTTRA) collaboration [1,2], whose activities are focused on the development and testing of uranium-free dispersion fuels for transmutation scenario's in light water reactors (LWR) or fast reactors (FR).

Transmutation of americium is a complex process of neutron capture, fission and decay reactions (Fig. 1), of which neutron capture leads to the formation of other actinides, including long-lived ones. The extent of fissioning of the produced actinides must be very high (>90%) in order to effectively reduce the amount of americium and to limit the production of curium. To achieve this, one has to optimise the neutron flux and neutron energy by choosing the highest available neutron flux and a thermalised neutron spectrum. One way of achieving this is moderating the neutron flux in a fast reactor. For such optimised conditions a once-through cycle could be sufficient. Alternatively, a multi-recycling scenario could be envisaged [3].

As a result of quasi-total incineration, a chemical 'revolution' of the fuel (i.e., a significant alteration in fuel composition) takes place. The americium initially present in the fuel will be first converted, in a relatively short period, into curium and plutonium isotopes by capture and decay reactions, while at the end of the irradiation only fission products will be present. Quasi-total incineration leads also to extreme irradiation conditions and hence, to a high level of damage to the matrix of the fuel. The goal of fuel matrix design is to create a support for the actinide phase to keep a good mechanical integrity and thermal conductivity throughout radiation. An extensive selection of matrix materials was made on the basis of logical criteria [4] and several materials were irradiated in reactor experiments. The most relevant of these is probably the EFTTRA-T4 experiment in which a fuel of 11 wt% Am, microdispersed in spinel, was irradiated to an

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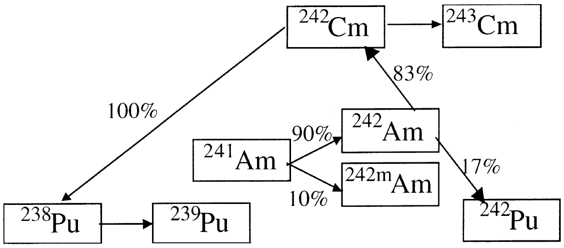

Fig. 1. Transmutation scheme for ^{241}Am in a thermal flux. In the present context, two points are relevant: (i) because of the very short half life of ^{242}Am ($t_{1/2} = 16$ h) most of it will decay to ^{242}Cm, though its fission cross section is high ($\sigma_f = 2900 \times 10^{-24}$ cm^2), and (ii) the decay product ^{242}Cm has a low fission cross section ($\sigma_f < 5 \times 10^{-24}$ cm^2) and decays with a short half life of 163 days, producing ^{238}Pu and emitting an alpha particle.

extent of transmutation of 92% and an extent of fissioning of 32% (results of post-test calculations). The estimated central fuel temperature was about 900 K. The observations after irradiation revealed significant swelling (18% in volume). This effect is due to the defects and the damage created in the matrix which are induced by neutrons, energetic fission fragments and alpha decay. Especially the latter two damage sources are of great importance. Recent work has shown that fission products at fission energy can cause amorphisation in spinel, which gives rise to significant swelling [5,6]. Swelling can also be caused by the He-atoms formed in the α-decays of Am and of the transmutation product ^{242}Cm. The helium production (and subsequent bubble formation) will be much larger than in standard fuel (Table 1). Supporting evidence is and in the future will be obtained from irradiation experiments using uranium as a simulant for americium (see Table 2).

The above noted problems can probably be limited by the choice of the proper target microstructure of the pellet, and of the matrix material and actinide compound. In this paper, we will present the considerations for the optimisation of inert matrix fuel concepts for americium transmutation with regard to the behaviour under irradiation and the performance for transmutation.

2. Dispersion versus solid-solution fuels

For the heterogeneous mode incineration, two types of fuels are generally considered: dispersion of the fissile phase in an inert matrix (inert neutronically) or a solid solution of the fissile phase in the matrix. Dispersion fuels were considered in the 1950s as a potential fuel for power stations [7,8], e.g. enriched UO_2 in steel (cermet type). Though positive results were obtained, sintered UO_2 pellets without any additives were selected for various reasons, including economic arguments and the very good in-pile performance of UO_2. However, for inert matrix fuels dedicated to transmutation, another support (matrix) for the actinides has to be found. For this support, new criteria have been defined which are different from those for standard fuel as only partial loading is envisaged, along with very long irradiation times. Therefore, the materials science demands are more stringent. For instance, good fuel properties (structural, thermal, mechanical) have to be maintained in spite of the radiation damage occurring at these extreme operating conditions.

Three sources of damage can be distinguished:

- neutrons;
- alpha decay (~5 MeV alpha particles and ~100 keV daughter-nuclide recoils);
- fission products (light and heavy ions of about 70–100 MeV).

The effects of these damage sources are different since the energy loss and range of energy deposition are different. Energetic neutrons cause isolated collision cascades throughout the material. Alpha decay causes largely isolated displacements along the range of the alpha particle (20 μm) and a very dense short (25 nm) collision cascade produced by the recoil atom (e.g. ^{238}Pu in the decay of ^{242}Cm) at the site of the decay. Fission creates two energetic fragments emitted in opposite directions each causing fission tracks of about 8–10 μm length. In fact, most atomic displacements will be caused by fission fragments.

In a solid solution this damage will be distributed homogeneously, whereas in a dispersion arrangement, the damage can be localised to a different extent depending on the size of the inclusions of the dispersed

Table 1
Fission gas and helium production in various fuels

Reactor type	Fuel composition	Burn-up (% FIMA [a])	Gas production [b] (cm^3 g^{-1} of actinide oxide)	
			Fission gases	Helium
PWR	UO_2	6.2	1.8	Very low
PWR	MOX	5.0	1.3	0.1
Fast reactor	MOX	17.5	3.6	0.15
Fast reactor	MgO + 20 wt% AmO_x	85	20.6	36

[a] FIMA (fissile initial metal atom) refers here to heavy metals (actinides) only.
[b] NTP (298.15 K, 1 bar).

Table 2
Relevant irradiation experiments for inert matrix fuels performed by the EFTTRA partners

Name [a]	Reactor	Description	Start (year month)	Length (EFPD) [b]	Extent of fission (%FIMA) [c]
T2	HFR [d]	Neutron damage in inert matrices	96.02	386.4	–
T2bis	HFR	Neutron damage in inert matrices	96.02	101	–
T3	HFR	Neutron damage in inert matrices	97.10	199	–
		Dispersion inert matrix fuel using enriched UO_2			18
T4	HFR	Americium in spinel	96.09	358	35
T4bis	HFR	Americium in spinel	97.06	>550	>60
T4ter	HFR	Central fuel temperature of spinel/UO_2	97.06	>550	>60
T5	HFR	Hybrid fuel for Am: influence of inert matrix	Planned	350	∼30
F1	Phénix	Neutron damage in inert matrices	94.12	61	–
MATINA		Dispersion inert matrix fuel using enriched UO_2			1.3
F1A	Phénix	Neutron damage in inert matrices	98.05	181	–
MATINA 1A		Dispersion inert matrix fuel using enriched UO_2			3.6
CAMIX	Phénix	Hybrid fuel: study of Am phase	Planned	400	∼30
COCHIX	Phénix	Hybrid fuel: optimisation microstructure	Planned	400	∼30
THERMHET	Siloé	Thermal behaviour of a composite fuel	97.10	42	1.3

[a] Some of the experiments are also known under different names such as RAS or MATINA.
[b] EFPD: equivalent full power day.
[c] FIMA: fissile initial metal atom.
[d] HFR: high flux reactor in petten (The Netherlands).
MATINA: MATrices for the Incineration of Actinides in the Phénix fast reactor, THERMHET: THERMal behaviour of HETerogeneous fuels in the Siloé experimental reactor, EFTTRA-T3: EFTTRA experiment of testing inert matrices under Thermal spectrum, COCHIX (Concept Optimized miCrostructure in pHénIX), CAMIX (Compounds of AMericium in phénIX) in Phénix fast reactor.

phase (Fig. 2). The radiation effects in dispersion fuels with very small inclusions will approach that of a solid solution; on the other hand the radiation effects in dispersion fuels with big inclusions will be concentrated in the inclusions while the matrix will essentially be subjected to neutron damage only (Fig. 3). Since radiation damage can cause severe deterioration of the matrix properties and since the bulk properties are determined by the matrix, the dispersion fuel concept is preferred for transmutation of americium in order to reduce the

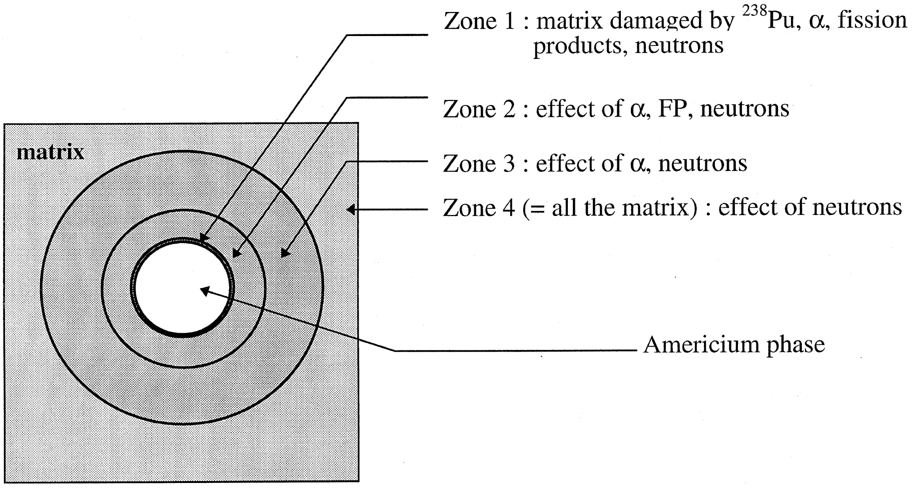

Fig. 2. Schematic presentation of the radiation damage in a dispersed fuel.

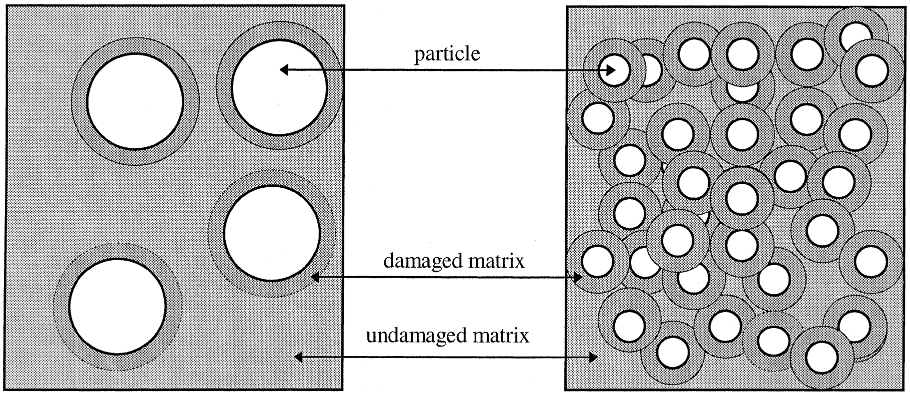

Fig. 3. Schematic presentation of the effect of particle size on the radiation damage shown as a projection onto a plane.

volume of the matrix that will be affected by damage processes and impurity (decay and fission products) ingrowth.

3. The americium phase

The ideal chemical form of the americium in the dispersion should be further explored. In case of an oxide fuel, americium dioxide and americium sesquioxide have unfavourable properties. They have low thermal conductivity [9], high oxygen potential [10,11] and high chemical reactivity towards many matrices [12]. Intermediate compositions, e.g. $AmO_{1.62}$ are preferred but their preparation is difficult since it requires accurate control of the conditions during the fuel fabrication process. Due to the high oxygen potential of AmO_2 (Fig. 4), it is very difficult to produce a fuel with stoichiometric americium dioxide. Even annealed in air, AmO_2 loses oxygen. If annealed under vacuum for example at 1343 K, AmO_2 decomposes to about $AmO_{1.65}$. The cladding (Zircaloy or steel) will keep the oxygen potential at about the values for UO_2, and use of an AmO_2 fuel would therefore cause inside clad corrosion.

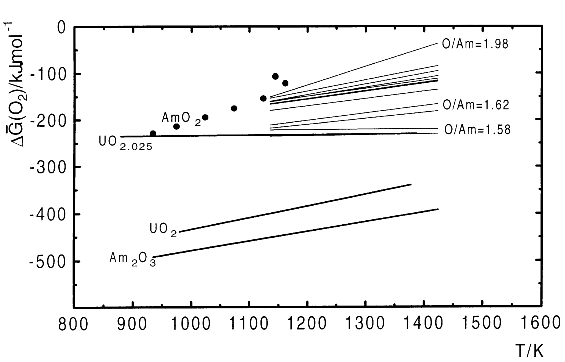

Fig. 4. Oxygen potentials of americium oxides as a function of temperature for O/M ratios of 1.98, 1.96, 1.90, 1.85, 1.80, 1.75, 1.70, 1.65, 1.63, 1.62, 1.59 and 1.58. For comparison, data points for AmO_2 and lines for $UO_{2.03}$ and Am_2O_3 are also shown. The lines for AmO_{2-x} are based on about 10 measurements each [10].

A solid solution of AmO_2 in, for example, ZrO_2 is therefore proposed as an alternative, assuming that such a solid solution leads to a stabilisation of the cubic phase (which alternatively could be obtained by addition of Y_2O_3) and of the O/M ratio and, hence, the valence state of Am. Recent experiments on the system $(U,Zr)O_2$ show that ZrO_2 effectively stabilises the fluorite structure and keeps changes in the valency of U in a limited range [13]. The same positive effect may be expected for the Am–Zr mixed oxide. The oxygen potential values for a mixed $(Zr,Am)O_2$ oxide are not known. We will call ZrO_2 the host phase.

For a nitride fuel, AmN can be considered, however, most of its properties are unknown. Nevertheless, its stability at high temperature is doubtful in view of the trend in the nitrides of the actinide series. Again, stabilisation in a host could be considered, e.g. in ZrN. This has to be experimentally confirmed.

4. The inert matrix

The selection of inert matrix for actinide fuels is carried out for oxides, nitrides and metals. A first evaluation was made on the basis of availability and price, basic properties (thermal conductivity, melting point, compatibility with coolant and cladding, etc.), radiation stability and neutron activation [4,14]. Within the EFTTRA collaboration, the current emphasis is on oxides and, to a much smaller extent, on nitrides and metals. Several selected materials are being tested by irradiation experiments in the reactor Phénix (France) and the High Flux Reactor (Netherlands). MgO, $MgAl_2O_4$, $Y_3Al_5O_{12}$, Y_2O_3, TiN and ZrN are the most important candidates. In Switzerland (PSI), Italy (ENEA) and USA (LANL) zirconia-based fuels are developed; in Japan (JAERI) complex mixtures of oxides, called ROX, are considered. In these later cases plutonium incineration is the goal.

For americium fuels some specific problems have to be addressed:

- analysis of the unirradiated fuel of EFTTRA-T4 (microdispersion of AmO_x in $MgAl_2O_4$) showed that a reaction between the americium oxide and aluminium occurred to form a new phase, likely to be $AmAlO_3$ [11]. Experimental studies have to confirm whether or not this compound is a suitable host for americium;
- due to alpha decay of the transmutation product ^{242}Cm, a considerable amount of helium will be produced during irradiation, as confirmed by a former irradiation in Phénix [15]. A similar problem has been predicted by pre-test calculations for EFTTRA-T4 [1].

At present it is not clear whether retention of helium in the fuel or high release in a specially designed pin (big plenum, vented pin) is to be preferred. In spite of the large knowledge of mechanisms for fission gas release from UO_2 and other ceramics, it is not straightforward to extrapolate this to the helium release from dispersion fuels due to large differences in mass and atomic size between He and Kr/Xe. Experimental programs to investigate this problem have been started, and their results will be used as additional criteria for further optimisation of the inert matrix.

5. The optimum microstructure

First the optimum form of the host particle must be chosen. Considering that a spherical particle has the lowest surface area compared to other shapes of similar volume for the same amount of particles, it is clear that spherical particles will lead to the least damage within the inert matrix. Particles with a small size are advantageous because their use limits the temperature gradient in the particle and in the fuel [16–18]. However, if the radiation damage in the shell around the host particle leads to a decrease in the thermal conductivity of the matrix, the anticipated lower temperature in a fuel with small particles is not realised and depends instead on the irradiation-induced decreases in the thermal conductivity [16–18]. In case this decrease is significant, large particles are advantageous since they reduce the volume of the matrix that is affected by radiation damage (Figs. 5 and 6).

The final choice of host particle size is a compromise. Calculations show that the optimal diameter is between 50 and 300 μm, the lower limit being determined by the sharp increase of the damaged fraction of the inert matrix (Fig. 5), the upper limit being determined by the temperature gradient in the host particle [16–18]. Optimisation has to be done on a case-by-case basis. Suggestions are given in Section 6 for planned irradiation experiments.

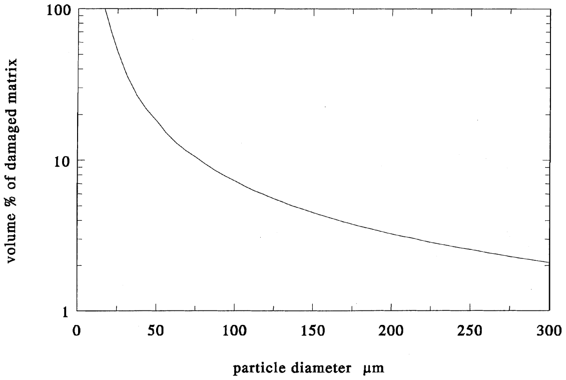

Fig. 5. The volume of damaged matrix as a function of particle diameter for MgO + 20 wt% AmO_x (Am density 0.83 g cm^{-3}).

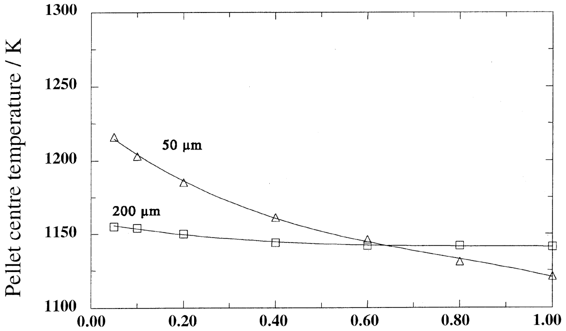

Fig. 6. Effect of the thermal conductivity on the pellet centre temperature. Conditions: MgO + 40 wt% Am; linear power: 100 W cm^{-1}; good thermal contact between matrix and particle (coefficient of heat transfert: 4.0 W cm^{-2} K^{-1}).

However, these calculations have been made for configurations in which the contact between host particle and inert matrix is good or even perfect. In practice this will not be the case. A poor contact (mechanical decoupling of the materials) will lead to a higher temperature gradient in the host particle but could accommodate the swelling of the host particle and will prevent propagation of stresses from the host particle to the inert matrix and vice versa.

Accommodation of swelling can also be achieved by introducing porosity, preferably in the host particle. Closed porosity may also help to retain the helium and fission gases in the host particle in case retention is preferred. In that case, a metal matrix would be beneficial since it prohibits diffusion of helium and provides a good thermal conductivity. However, the helium pressure in and around the host particle would become very high. If release is preferred, a solution might be the introduction of some porosity in the inert matrix as well. In that case 10% porosity seems to be sufficient as at that level a network of open porosity is expected without reducing too much the thermal conductivity of the inert matrix. This could also be achieved in a sphere-pac of host and inert-matrix particles. In addition to the effects on material properties, the choice between these concepts depends on technology requirements, but both large complete retention and large complete release of fission gases have been used with success in LWRs and FRs, respectively.

6. Conclusions

From the above discussion it was found that an optimised fuel for efficient americium transmutation requires an inert matrix as well as a second host phase. This so-called hybrid fuel combines the advantages of the dispersion and solid solution concepts. For a fast reactor MgO and (Zr,Am)O_{2-x} seem to be the most appropriate materials for the inert and host material, respectively. An alternative may be a combination of TiN as inert and (Zr,Am)N as host matrix. For LWRs, MgO or nitride fuel are not accepted because of their reactivity with water, leaving $MgAl_2O_4$ and $Y_3Al_5O_{12}$ as inert matrix materials for fuel pellets, though these have been shown to react with americium [19]. The hybrid fuel concept has therefore to be modified. The following possibilities exist:

- to use ZrO_2 as inert matrix but this will limit the maximum americium content that can be used, because of the low thermal conductivity of ZrO_2;
- to coat (Zr,Am)O_2 particles with for example ZrO_2 and use $MgAl_2O_4$ as the inert matrix;
- accept $AmAlO_3$ as host phase in combination with $MgAl_2O_4$ as the inert matrix.

This hybrid concept and the proposed modifications will be further explored. It is clear that in order to achieve a final solution a considerable amount of research is required. The following areas are identified as crucial:

1. *Fundamental properties of the potential americium host phases*. Knowledge of the phase diagrams of the potential host phases, ZrO_2–Y_2O_3–AmO_{2-x} (possibly Al_2O_3–AmO_{2-x}) and AmN–ZrN, is of importance to verify the existence of a cubic phase in an acceptable composition range. Next, physical properties (e.g. thermal conductivity, dissociation pressure, etc.) of the host phases should be measured in order to predict the thermal behaviour of the fuel. At the same time, the radiation stability of the host phase should be investigated out-of-pile to permit a prompt assessment regarding the efficiency of proposed designs. α-decay damage can be studied with Am-doped phases and fission product damage can satisfactorily be simulated in accelerators with fission product ions of fission energy [5,20].
2. *Development of fabrication techniques for hybrid fuels containing americium*. This was not addressed in the preceding Sections, and it is an essential aspect of the feasibility of the inert matrix concept. Mixing of spheres prepared by a sol–gel method, with powder of the matrix phase seems to be promising, though some practical problems have been identified [21]. However, this method is complex and handling of the highly radioactive americium is necessary in all steps of the process, especially when a ZrO_2 coating of the spheres is necessary to prohibit reaction with the matrix. Methods like coprecipitation, powder blending or infiltration are simpler but have serious disadvantages, of which the most important one is the absence of control of sphere size and form of the particles. It is anticipated that the ongoing activities will provide an adequate solution in the near future.
3. *Irradiation tests of the in-pile behaviour of fuel components* (*inert matrix*, *host material*) and fuel. An extensive programme of irradiation tests of fuel components and fuels has been started by the partners of the EFTTRA collaboration and the results of some of these experiments have been discussed in the preceding sections. Table 2 gives a summary of the EFTTRA irradiation program. The hybrid fuel

Table 3
Suggested priorities for R&D work on the host materials for the hybrid concept, the suggested matrix is $MgAl_2O_4$ spinel

R&D activity		Items	Priority
Phase diagrams		ZrO_2–AmO_2, AmN–ZrN	1
Thermal properties	Thermal conductivity Melting point Dissociation pressure	AmO_{2-x}, $(Zr_{1-y},Am_y)O_{2-x}$	3
Radiation stability	α-decay Simulated fission	ZrO_2, ZrN	1
Fabrication hybrid fuel		Optimisation of the process	2
Reactor behaviour		Influence of microstructure Influence of temperature	3

concept, as outlined in this paper, will be the subject of future tests.

In Table 3 the requirements for research are summarised, and priorities assigned. This serves as a guideline for our future work.

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