"The GIOCONDA experience of the Joint Research Centre Ispra: analysis of the experimental assemblies finalized to their safe recovery and dismantling"

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Abstract*

The management of the irradiated nuclear fuels is considered a fundamental step in the global strategy of the Ispra site's nuclear liabilities elimination prior to the decommissioning of the ESSOR reactor.

In this frame, the unit Nuclear Decommissioning and Facilities Management of the JRC Ispra has conducted a study on the recovery and safe dismantling of the four experimental nuclear assemblies, coming from the past so-called GIOCONDA experiments. The assemblies, containing a Na-K (44–56% in weight) alloy and now stored in waterproof rigs, were utilised to investigate on the thermal behaviour of UO_2 fuel pellets and compacted micro spheres under irradiation.

The study highlights the risks linked to handling, manipulation and dismantling of the assemblies, separation of the components, Na-K alloy neutralization, irradiated fuel separation and segregation, resulting radioactive waste management. Also, the possible consequences on workers and structures have been considered in normal and accidental conditions.

After a brief description of physical and chemical characteristics of Na-K, a detailed analysis is performed with the aim to predict the present physical and chemical status of the eutectic alloy and the related content in terms of TNT-equivalent mass, by using semi-empirical techniques supported by mathematical methods.

The study ends with a "worst case analysis", with the aim to evaluate the mechanical consequences on ESSOR pond structures and the radiological consequences on workers and public health in the event of an accident due to the Na-K alloy explosion.

KEYWORDS: **experimental rigs, recovery, NaK alloy, reactivity, oxide layers model, worst case analysis.**

1. The GIOCONDA experience: brief description of the experimental rigs

The GIOCONDA experience was carried out in the '70s and '80s in the frame of an agreement between the European Commission and the Italian government.

The research was focused on the thermal behavior of a fuel rod under neutron irradiation. In particular, measurements of the conductivity integral and the thermal conductance between fuel and cladding were carried out, with linear power up to 650 W/cm and outer temperature of the cladding of 300˚C. The irradiation tests were conducted in the so called MODESTE device in channel n. 8 of the ESSOR reactor.
The rig has a complex cylindrical geometry, made up of coaxial capsules with a total length of 4700mm and an external diameter of 65mm.These are considered as multiple barriers for the NaK alloy.

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The rig consists of an active part, which was irradiated in the reactor core, and a structural upper part, including the shield and the connexion head.
The active part includes a γ-calorimeter and the capsule.
The capsule in made up of a Zy-2 inner tube (Ø 18x20mm) containing the fuel rod, and an outer Zr-2 tube (Ø 36x38mm), cooled by the heavy water of the ESSOR reactor.

The gap between the inner and outer tube is filled with a **NaK** metal alloy (44-56% weight), up to 38cm over the upper limit of the fuel, for a total of 125 cm^3 liquid volume, the remaining part of the tube being filled with helium. Around the inner tube two heat resistances are wrapped for calibration and temperature control purposes. Outside the heat resistances, a measuring resistance is fixed, its value depending univocally on its average temperature (axial and radial).
The inner tube is fixed to the rig by means of a tight shielding plug with openings for thermocouples (for rod and NaK), a pipe for NaK filling and a pipe for tube pressurization. The external instrumentation of the capsule enters the rig in its upper part, reaching the so called rig head, whose inner volume is filled with helium.

The fuel rods utilized for GIOCONDA experience were of twp types: 1) pellets, in rigs #1 and 2; vibro-compacted micro spheres in rigs #5 and 6.

2. Phases envisaged for the recovery and dismantling of rigs

The recovery of the GIOCONDA rigs is part of the general decommissioning strategy, which envisages the realization of an interim store for the irradiated fuel in the ADECO hot cells of the ESSOR reactor.
The present arrangement of the rigs and the configuration of the ADECO building, containing the pool and the hot cells, represent the technical constraints of the operating phases for the recovery that have to be developed taking into account the identification of the related problems.
Moreover, the reduced size of the active part and the presence of the NaK alloy, representing two conflicting aspects of the same problem, make the analysis for the recovery of rigs highly complicated. In fact, although the reduced dimensions of the fuel part (15cm) allow the hypothesis of having an advantageous reduction in waste volumes, with subsequent separation of highly active waste, the presence of the NaK, highly reactive with air and water, implies the need of precautions during the rig handling.

The following is a proposal of an operating procedure for the recovery of the GIOCONDA rigs with the identification of the main phases:

2.1. Rigs characterization

This phase entails the following points:
- Retrieval of design information, including geometry and nature of components;
- Irradiation history: irradiation in-core cycles, burn-up, decay time etc.
- Need of NDA examinations on rigs, in order to get detailed information on current state and level of the alloy as well as fuel integrity.

The first two objectives have been successfully performed by means of an exhaustive search in the ESSOR reactor archives.
The need of NDA examinations on rigs and also the type of examination will depend on a cost-benefit analysis linked to the effective possibility of moving the rigs. In fact, the presence of oxidized layers on the free surface of NaK could prevent a direct handling of rigs in the pool because of the high risk of explosion. As a consequence, it is evident that an underwater test in the pool can be more onerous and expensive that one performed in the hot cell.
The following NDA tests have been considered for the characterization phase:
- Gamma spectrometry, to investigate on fuel irradiation ,fission products concentration and spatial distribution. Many dry and underwater tests have been done, so that its realization is linked more to its real utility than to its feasibility.
- X radiography to investigate on components of rigs as well as on the detection of "anomalies" in the cladding. Unfortunately, the execution of underwater tests of such method have not been reported yet in technical literature.

- Eddy currents method, with the aim to determine the presence of NaK oxides layers.. However, the necessity to have direct access to the rig head (opening of the storage containers) and the availability of small size detectors make this method of difficult applicability to the GIOCONDA rigs.

2.2 Transfer of rigs from pool to ADECO hot cell 4411

This phase has the objective to transfer the rigs from the pool to the hot cell for successive operations of NaK removal and rig dismantling.
It has been determined that the hot cell 4411 is the most suitable place for the above operations, due to the radiation dose rate of rigs and to the necessity of processing a highly reactive alloy in a confined area.

For the safe accomplishment of this phase, it will be extremely important to determine the NaK state of conservation in the capsule.
In fact, it must be underlined that the movement of rigs can have, as a consequence, the "washing" of the NaK oxides surface layers with the underneath liquid alloy, originating highly exothermic reactions. Therefore, in the next chapter 3 a chemical analysis and a theoretical evaluation of the status of oxidized species on the surface of NaK in the capsule will be performed with the aim to predict the status of the alloy in the capsule.
This analysis will justify, a priori, the need for exceptional operations to be integrated in the normal procedures of fuel handling in the pool.

2.3 Extraction of the experimental fuel from rigs and separation from structural parts

This phase, to be conducted in the hot cell in inert atmosphere (helium or argon), consists on the extraction of the experimental fuel from the rig and its subsequent washing to eliminate traces of NaK. It is envisaged the production of a certain amount of HLW (fuel) as well as medium and low activity solid (rig structural parts) and liquid (from washing) waste.

2.4 Nak removal

This phase envisages the emptying of 450g of NaK from the capsules in specific pots. The alloy recovery can be carried out "by gravity" through perforations on the equipment.
After recovery, the final destination of the alloy must be considered. Two are the possible alternatives:

- Nak neutralization in the hot cell;
- Transportation of the alloy in suitable containment/transportation means to an off-site processing facility.

The choice has to be done taking into account the total NaK quantity to neutralize (or to transport) and the real technical feasibility of such neutralization in a hot cell.

2.5 Final washing

This phase has the scope to eliminate all traces of NaK. In fact, the emptying process does not allow the complete removal of the alloy from the capsule.
The washing can be done with water or alcohol, ensuring at the same time a controlled oxidation reaction of the residual NaK.

3. <u>NaK management</u>

The strategy for the recovery of the GIOCONDA rigs has put into evidence the difficulties in the management of the NaK alloy. This means that the feasibility of a recovery project should start from the necessary acquisition of know-how on alkali metals handling, specifically sodium-potassium alloy handling.

3.1 Physical properties of NaK alloys

The term NaK refers to the metal alloy of sodium and potassium at different weight percentages. In the specific case of GIOCONDA, NaK-56 is an alloy with a weight composition of 56% potassium. The "classic" equilibrium diagram of NaK is shown in the slides, while Table 1 hereafter summarizes the physical properties.

Table # 1: Physical properties of sodium and potassium alloys

	Melting Temperature(˚C)	Boiling Temperature (˚C)	Density at 20 ˚C (g/cm^3)	Thermal conductivity (W/cm ˚C)
Na	97,8	881	0,968	0,86 (100˚C)
K	63,7	756	0.855	0,52 (100˚C)
NaK-78	-12,6	785	0,87	0,232 (100˚C)
NaK-56	6,9	812	0,898	0,216 (50˚C)
H_2O	0	100	1	0,007 (100˚C)

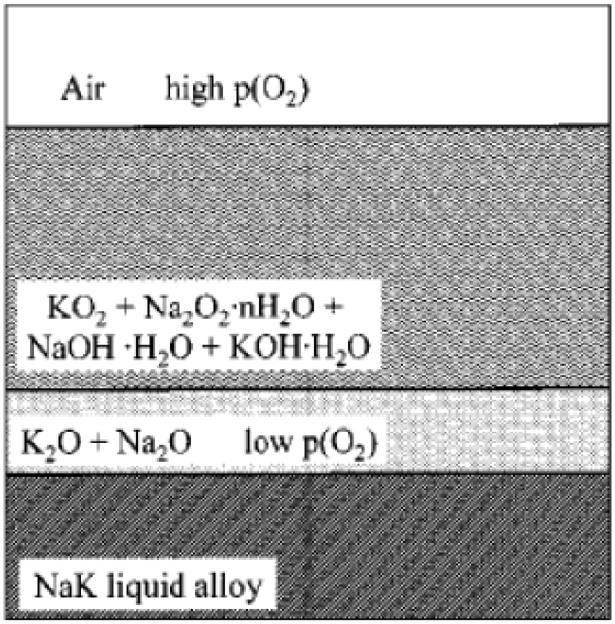
3.2 NaK oxidation and potential risks

The chemical reactions of NaK are those of alkali metals, for which special safety measures must be taken, because of their high reactivity with several materials of common use.
As already anticipated, the oxidation of NaK plays a significant role in the realization of the recovery project of GIOCONDA rigs, because of the potential risks of explosions also at room temperature.
The thermodynamic analysis of the reactions NaK-water vapor-oxygen as well as the experimental campaigns carried out with the aim to study the behavior of NaK with its several oxidized species, lead to the conclusion that very fast exothermic reactions, sometimes at room temperature, are always due to the presence of a surface porous matrix containing super oxides and hydrated hydroxides.
As a result of the contact with the underneath liquid alloy, these species originate hydrogen and heat, leading to the decomposition of the super oxide KO_2, with release of Oxygen. Thus, it is the presence of this particular super oxide to make very difficult the management of NaK, also at room temperature.

3.3 Model of the NaK oxide layers applied to the GIOCONDA rigs

According to the information gathered from the chemical processes involved, the theoretical behavior of the chemical compounds, supported by operative experience in ESSOR reactor, in other European research laboratories as well as in in-field industrial operations, a model of NaK oxide layers to be applied to the GIOCONDA rigs can be developed. Although the model is theoretical, we believe that it is very likely to approach the real situation inside the capsules.
As seen before, the predominant chemical species in presence of an excess of Oxygen are the sodium peroxide Na_2O_2 and the potassium super oxide KO_2, while in direct contact with the liquid alloy, and therefore, in excess of metal, simple oxides Na_2O and K_2O are likely to be present.
Although all oxidized compounds have densities higher than the metal alloy and their precipitation should be expected, it has been found that the oxides are always at the surface of the NaK metal alloy, producing oxidized layers with porous matrix.
In addition, it must be mentioned that some oxidized species show high hygroscopic behavior. Therefore, even in presence of traces of water it is plausible the presence of hydrated compounds like $\mathbf{Na_2O_2 \cdot 8\ H_2O}$, $\mathbf{Na_2O_2 \cdot 2\ H_2O}$, $\mathbf{KOH \cdot H_2O}$ and $\mathbf{NaOH \cdot H_2O}$. The presence of traces of water and oxygen is justified by the fact that they could be present in helium used to fill the plenum of the capsules.
In these conditions, the oxide layer can emerge from the alloy surface, preventing, de facto, in the upper part the reduction of the potassium super oxide and the sodium peroxide by means of the underneath alloy.
In conclusion, the **proposed stratified model** is shown in Fig. 1, where simple oxides of sodium and potassium produce a layer keeping separate the liquid metal alloy from the upper super oxides layers.

Figure # 1: proposed stratified model for NaK



With such a model, it has been possible to identify the starting event of accidental explosions occurred in the past during handling operations on NaK at room temperature: the accidental contact of the external super oxides layer with the underneath liquid metal alloy.
Such a contact originates the extremely exothermic reduction of the potassium super oxide, according to the following reaction:

$$2KO_{2(s)} + 2K_{(l)} = 2K_2O_{(s)} + O_{2(g)}, \Delta G^{\circ}{}_{298} = -164 KJmol^{-1};$$

$$2KO_{2(s)} + 2Na_{(s)} = K_2O_{(s)} + Na_2O_{(s)} + O_{2(g)}, \Delta G^{\circ}{}_{298} = -220 KJmol^{-1};$$

Moreover, assuming that the compounds of the floating porous surface layer are hydrated, their contact with the liquid metal NaK can induce additional highly exothermic:

$$Na_2O_2 \bullet 8H_2O_{(s)} + 8Na_{(l)} = Na_2O_{2(s)} + 8NaOH_{(s)} + 4H_{2(g)}, \Delta G^{\circ}{}_{298} \approx -1000 KJmol^{-1};$$

$$NaOH \bullet H_2O_{(s)} + Na_{(l)} = 2NaOH_{(s)} + 0.5H_{2(g)}, \Delta G^{\circ}{}_{298} = -132 KJmol^{-1};$$

$$KOH \bullet H_2O_{(s)} + K_{(l)} = 2KOH_{(s)} + 0.5H_{2(g)}, \Delta G^{\circ}{}_{298} \approx -130 KJmol^{-1}.$$

A diverging reaction could release more and more heat, fostering the further decomposition of KO_2 with additional oxygen release. In such conditions, the explosive reaction between hydrogen and oxygen could be unavoidable:

$$2H_{2(g)} + O_{2(g)} = 2H_2O_{(g)}, \Delta H^{\circ} = -483 KJmol^{-1}$$

It has been experimentally demonstrated that <u>explosions are due to the presence at the same time of hydrated compounds and potassium super oxide in the floating upper layer</u>.

As a conclusion we can state that also the simple movement of the rigs and the metal alloy is able to initiate an explosive reaction even at room temperature, so to produce the contemporaneous release of heat, hydrogen and oxygen.
It goes without saying that the severity of the reaction and its consequences depend on the degree of hydratation of the sodium peroxide and the hydroxides.

3.4 Calculation of the mass of oxide layers in the GIOCONDA rigs

On the basis of the above model and the considerations on possible accidents due to the simple movement of the alloy, **a calculation of the mass of oxide layers in the capsules** of the GIOCONDA rigs has been performed, with the aim to determine the real "explosive load" and, as a consequence, the need for exceptional handling procedures in the pool and in the hot cells.
Taking into account the following conservative yet realistic hypotheses:

- V_{NaK} = 125 cm^3 V_{plenum} (dry air only) = 654 cm^3 ρ_{Air} (0°C, 1atm) = 1,3 g/dm^3
- All gaseous oxygen in dry air (≈ 23% in weight) is available for the oxidation of the NaK alloy. Then, the oxygen mass which could oxidize the sodium and potassium is

  M_{air} = 1,3 g/dm^3 · 654 · 10^{-3} dm^3 = 0,85g → **M_{O2} = 0,23 · 0,85 = 0,1955g**

  → **n_{O2}** = 0,1955/32 = **6,11 · 10^{-3} mol**

- The two macro-reactions (oxidation of sodium and potassium leading solely to stable NaK oxides) are equally thermodynamically fostered, due to the fact that their ΔG has almost the same value (-900KJmol^{-1}). This allows to consider that half of oxygen total molar mass be available for each macro-reaction: n_{O2} = 6,11·10^{-3}/2 = **3,055 ·10^{-3}mol**.

This assumption lead to an overestimated quantity of sodium peroxide that, together with the potassium super oxide, must be considered the most critical specie in terms of release of gaseous hydrogen and oxygen. Thus, the oxide layer is made up of only sodium peroxide and potassium super oxide. Considering the oxidation reactions in sequence, from stoichiometry we have:

3 : 2 = 3,055 ·10^{-3}mol : n_{K2O} → n = **2,04 ·10^{-3}mol**

2 : 2 = 3,055 ·10^{-3}mol : n_{Na2O2} → n = **3,055 ·10^{-3}mol**

- As we have assumed that all oxygen in the plenum has been used to produce the macro-reactions, then the peroxide can be considered in his superior hydrated form. This means that, in case of oxide layer washing, we'll have the maximum possible release of hydrogen.

Then, the accidental scenario is the following:

$$2KO_2 + 2K \rightarrow 2K_2O + O_2;$$
$$2KO_2 + 2Na \rightarrow K_2O + Na_2O + O_2;$$
$$Na_2O_2 \cdot 8H_2O + 8Na \rightarrow Na_2O_2 + 8NaOH + 4H_2;$$
$$2H_2 + O_2 \rightarrow H_2O - 483KJmol^{-1},$$

It is evident that, starting from the calculated molar masses and the stoichiometry balances, the assumed dynamics could lead to partial combustion of hydrogen. However, in order to be conservative at the maximum possible extent, it has been imposed the complete combustion of H_2, by supposing that, due to oxidized NaK handling, it come in contact with air. According to this hypothesis, the critical mass is only the molar mass of hydrogen:

$$Na_2O_2 \cdot 8H_2O + 8Na \rightarrow Na_2O_2 + 8NaOH + 4H_2;$$
$$\Rightarrow 1:4 = n_{Na_2O_2 \cdot 8H_2O} : n_{H_2} \Rightarrow n_{H_2} = 1.22 \cdot 10^{-2} mol;$$
$$\Rightarrow M_{H_2} = 2 \cdot 1.22 \cdot 10^{-2} = 2.44 \cdot 10^{-2} g.$$

In order to have an energy information related to an explosive combustion, involving all the hydrogen mass, we have utilized the **"Method of equivalent TNT mass"**.

$$\mathbf{M_{TNT}} = \eta \cdot \frac{M_{H2}\,[kg] \cdot Q_{H2}\,[kJ/kg]}{4960\ kJ/kg} = \frac{2{,}44 \cdot 10^{-5}\,(kg) \cdot 241{,}5 \cdot 10^{3}\ kJ/kg}{4960\ kJ/kg} = \mathbf{1{,}256g}$$

where:
Q_{H2} is the combustion heat per unit mass of hydrogen;
η is a factor ≤ 1 due to the fact that not all the combustion energy is transformed in mechanical energy;
4960 kJ/kg is the energy released by 1kg of TNT.

4. Worst case analysis: explosion in the pool, causes, evolution and consequences

A complete assessment of the NaK handling and management must take into account the most severe accident that could happen during the operations, so to predict its causes and evolution and to evaluate the mechanical consequences on structures and radiological consequences on workers and environment.

The maximum accident foresees the sudden break of rigs during operations, with the subsequent quick reaction of NaK with water leading to a complete combustion of hydrogen released in air.
The concerned reaction is:

$$NaK + 2\,H_2O \rightarrow NaOH_{(s)} + KOH_{(s)} + H_{2(g)} + Q_H\ (6{,}8\ kJ/kg)$$

determining the quantity of hydrogen released.
Then, assuming a complete mixing of hydrogen with the oxygen in the air of the pool building and the presence of a primer, we have calculated the energy released in the explosion, considered as a "Confined Vapor Cloud Explosion" (CVE), by means of the method of TNT mass equivalent.

$$2H_2 + O_2 \rightarrow 2H_2O + Q\ (-483\ kJ/kg)$$

Other input data are:

PM_{Na} = 23 u.m.a.
PM_K = 39 u.m.a.

$V_{NaK} = 125\ cm^3$

ρ_{NaK} (20°C) = 0,898 g/cm^3

ρ_{H2} = 0,09g/*N*l

$PM_{NaK} = 0{,}44 \cdot 23 + 0{,}66 \cdot 39 \approx 31$

n_{NaK} = 450/31 = 14,52 mol

$M_{H2} = \rho H2 \cdot V_{H2} = \rho_{H2} \cdot nRT/p$ = 29,34g assuming the H_2 as ideal gas.

$$\mathbf{M_{TNT}} = \eta \cdot \frac{M_{H2}\,[kg] \cdot Q_{H2}\,[kJ/kg]}{4960\ kJ/kg} = \frac{29{,}34 \cdot 10^{-3}\,(kg) \cdot 241{,}5 \cdot 10^{3}\ kJ/kg}{4960\ kJ/kg} \approx \mathbf{1kg}$$

This figure has been introduced, as input data, in code EUROPLEXUS, developed by the JRC and the CEA, with the aim to assess the evolution of the explosion and the mechanical response of structures to the shock waive.

The results of the analysis clearly show that the accident can be a serious concern only for the operators working in the pool building. In fact, there's no possibility for the shock wave to spread over the pool structures. In addition, the dynamic strain due to the explosion has a minimum impact on the steady state of structures. The displacements, during the transient, are of the same order of magnitude (maximum some cm) of those of the transient simulating the pool building just under the sole gravity force.