

Technical note

Risks of explosion associated with "red oils" in reprocessing plants

This note presents the risks of explosion associated with reactions between TBP (tributylphosphate), its degradation products and nitrates derived from nitric acid or associated with heavy metals (uranium and plutonium), leading to the formation of unstable compounds known as "red oils". Feedback from explosions associated with the formation of these compounds, occurring in reprocessing plants around the world, is dealt with concisely. The main measures for controlling these risks implemented in the French plants concerned are also presented.

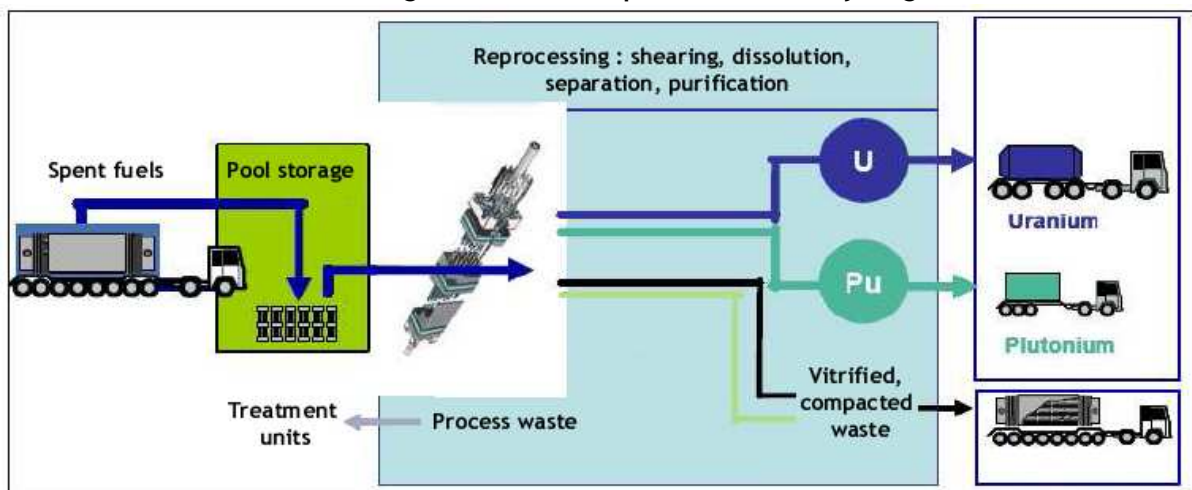
The PUREX process

The spent fuel removed from the core of a nuclear reactor still contains about 95% of uranium and 1% of plutonium. The main mission of reprocessing plants is to recover these nuclear matters in order to recycle it into new fuel. So, in these plants, the uranium and plutonium from the spent fuels are separated from the fission products and other actinides and packaged for interim storage before subsequent reuse, notably to make MOX fuel (MELOX plant in France), used in PWRs. The non-useable waste or "final waste", i.e. fission products and hulls and assemblies end-pieces, are specifically packed to ensure optimum safety (vitrifying stabilised waste and compacting metallic waste).

The PUREX process has become the process quite generally used for reprocessing slightly enriched uranium fuel from power reactors. The assemblies are first of all sheared into a few cm lengths, which fall into a dissolver with hot nitric acid. The acid dissolves the oxides of uranium and plutonium and most of others elements contained in the fuel inside zircaloy cladding. The undissolved "fines" are separated by centrifugation from the dissolver solution. The dissolver solution is then transferred to a chemical separation facility. In an array of mixers and settlers and pulsed columns, a solvent (tributyl phosphate diluted in an inert diluent) captures the heavy elements (uranium and plutonium) without extracting the fission products. The same principle is used to separate the uranium from the plutonium. The uranium is then purified and concentrated in liquid form (uranyl nitrate). The purified plutonium is transformed into a powder (plutonium oxide). These matters are then available to be used again, i.e. recycled as new fuel in nuclear reactors.

The particular risk linked to the formation of "red oils" is met in the chemical separation facility.

Processing of uranium and plutonium for recycling



Mechanisms of formation of "red oils"

TBP and its inert diluent (kerosene, n-dodecane, TPH¹ etc), as well as the products of their degradation by hydrolysis and radiolysis (DBP, MBP, phosphates, alcohols etc), are likely to react violently with oxidising products. At high temperatures, in the presence of nitric acid or nitrates of heavy metals (uranyle nitrate, plutonium nitrate), these organic compounds can lead to the formation of complex nitrous compounds called "red oils" (their red color is attributed to the nitrous compounds in the diluent), liable to decompose in an explosive reaction when the temperature of the mixture exceeds 130°C. Several explosions of this nature have occurred worldwide, the most significant being in the plants at Savannah River, USA (1953 and 1975) and Tomsk, Siberia (1993).

In the PUREX process, which is employed in reprocessing plants in France, this particular risk is chiefly met in evaporators which concentrate the aqueous flows from the different extraction/purification cycles containing nitrates (nitric acid and/or uranyle and plutonium nitrate) and traces of organic solvents in varying quantities which are a function of the efficiency of the treatments applied upstream on the different aqueous flows. The main units involved are the "intercycle" concentration units, where uranyle nitrate solutions are concentrated, the fission product concentration and acid recuperation units, where the raffinates from the various extraction cycles are concentrated, and the oxalic mother liquor treatment units. In these evaporators, the residual solvent (and its degradation products) is partly drawn off with the steam and condensates. The remaining fraction reacts with the nitrates present to form nitrous compounds - "red oils" - or breaks down thermally. The fraction of complexed solvents is greater if the quantity of heavy metal nitrates and nitric acid in solution, the degree of concentration and the temperature are high. This organic phase progressively saturates in heavy metal nitrates until its density becomes higher than that of the aqueous solution (1.1 to 1.6 g/cm³). These compounds will then accumulate at the bottom of the evaporator by a phase inversion phenomenon.

These reactions, which require prolonged heating, are nonetheless extremely complex (hydrolysis, oxidation and nitration reactions, radiolysis etc) and depend not only on the level of nitrates and the temperature of the medium, but also on the level of radiolytic degradation of the solvent, the nature of the diluent and the possible presence of a third phase or interphase precipitates or impurities² (phosphates etc), while the type and geometry of the evaporator may also be involved in the conditions of formation of "red oils". In particular, these compounds form much more easily when the diluent is composed of kerosene containing impurities such as aromatic compounds or alkenes, than when it is composed of n-dodecane or TPH (the diluent used in French reprocessing plants) not containing aromatic compounds. Data published in the literature indicate that "red oils" can decompose thermally above a temperature range of 130°C to 150°C, or even above 170°C, depending especially on the nature of their diluent and on their volatile organic compound content. This decomposition reaction, which displays first order kinetics, becomes extremely exothermic and autocatalytic above 135°C (the most penalising TBP/kerosene mixtures), and can be considered to be a thermal runaway in the absence of an adequate cooling source, and may lead to very high overpressure in the evaporator. This temperature threshold can be much higher for TBP diluted in dodecane or TPH. The potentially inflammable reaction products are composed of CO, CO₂, NO, N₂O, N₂, O₂ and volatile organic products (butyl nitrate, butyric acid etc).

¹ Hydrogenated tetra-propylene.

² Interphase impurities: precipitates which form and accumulate at the interface between the aqueous and immiscible organic phases in liquid-liquid extraction devices (decanter), composed especially of solvent degradation products and dissolution fines, which passed through the clarification stage.

The main accidents in reprocessing plants associated with the formation of "red oils"

The 1953 explosion in the Savannah River reprocessing plant, during a trial to concentrate a solution of hexahydrated uranyl nitrate by evaporation, was connected with the absence of adequate monitoring devices for the operation, which led to the erroneous estimation of the temperature in the evaporator and excessive evaporation of the solution (which had practically dried out). This excess evaporation caused violent thermal decomposition of the TBP/nitrate compounds present in the evaporator (36 litres of TBP were unexpectedly present in solution) followed by an explosion. The equipment was totally destroyed and the building was seriously damaged.

The same year, the same type of scenario occurred in the Hanford reprocessing plant, due on this occasion to an undetected fault in the evaporator's uranyl nitrate supply pump. Evaporation continued normally without modification of heating power, until the nitrate salts began to calcinate, with 40 litres of TBP initially present in the solution. However, the consequences of the explosion were less important, in view of the presence of a blowout diaphragm on the evaporator.

In 1975 a new explosion occurred in the Savannah River plant, during an operation to convert a concentrated solution of hexahydrated uranyl nitrate into UO₃ by denitration in the presence of an anti-foaming agent. 120 litres of TBP were transferred into the denitrator in an uncontrolled manner with the uranyl nitrate solution, after passing through two evaporators. The reaction runaway caused the temperature in the evaporator to increase from 250°C to 400°C, producing large quantities of inflammable gas and vapours and an explosion, despite the triggering of the emergency ventilation system. This explosion caused the destruction of the room containing the equipment, and damage to part of the building.

Finally, the explosion at the reprocessing plant in the Tomsk-7 industrial complex on 6th April 1993 led to major releases in the environment (about 20 TBq of α and β emitters). The accident was set off by an operation to adjust 25 m³ of partly decontaminated solution of U and Pu nitrates, in a 35 m³ vessel, using concentrated nitric acid (addition of 1.5 m³ of HNO₃ 14 N). However, this vessel also contained about 0.5 m³ of spent solvent and interphase impurities. This equipment was not stirred and since only the lower part had cooled, the addition of acid led to the formation of three phases: a first heavy phase composed of an aqueous solution of uranyl nitrate ([U] 400 g/L; 1.48 to 1.59 g/cm³), a second phase composed of spent solvent (1.4 g/cm³ in a layer 8 cm deep), and floating above this, a third phase composed of concentrated nitric acid (1.39 g/cm³). As the temperature of the upper part of the aqueous solution of uranyl nitrate reached 78°C, the layer of degraded solvent gradually heated up until it reacted uncontrollably with the concentrated nitric acid. In addition, the lack of stirring in the vessel and a relief valve in the closed position, due to an error following a maintenance operation, contributed to the thermal runaway of the reaction. The pressure in the top of the vessel reached 17 bars in 6 minutes, which caused the explosion and the rupture of the vessel, and the release of 250 m³ of inflammable gas and vapour. A second explosion caused the destruction of part of the structure of the building, leading to the release of around 10% of the vessel's radioactive content into the environment.

The feedback from these different accidents underlines the importance of total management of the parameters which ensure control of the content of the organic phase in aqueous solutions for concentration, as well as the evaporation temperature and conditions of ventilation in evaporators or concentrators, in order to control the risks of explosion associated with the formation of "red oils".

Measures implemented in the French reprocessing plants to prevent risks of explosion associated with "red oils"

In the French reprocessing plants, the risks of explosion from "red oils" are mainly associated with evaporators in units:

- for intercycle concentration which concentrate re-extraction solutions of uranium from the first extraction cycle³, before their transfer to the second uranium extraction cycle ;
- for concentration of fission product solutions from the first extraction cycle;
- for recovery of tritiated and non-tritiated acid where aqueous acid solutions of low and medium activity are concentrated;
- for treatment of oxalic mother liquors which concentrate mother liquors before recycling upstream of the phase of oxalic precipitation of plutonium;
- for treatment of organic effluents by distillation.

As stated above, the conditions for the appearance of risks associated with TBP/nitrate reactions which have been adopted in the safety analyses of the units referred to are:

- a temperature higher than 135 C in the evaporators;
- the presence of important quantities of TBP (and its degradation products) in the aqueous phase to be concentrated.

The main measures implemented for each item of equipment above are as follows.

- To limit the TBP content of aqueous solutions supplying the evaporators, the supply vessels of the units concerned are fitted with solvent flushing devices to separate, by decantation, any TBP drawn into these solutions, and the various aqueous flows from the extraction cycles are washed with diluent in batteries of mixer-decanters or in a centrifugal extractor (the process employed at Savannah River did not provide for a similar washing phase); feedback from operation of the installations shows that these measures allow the TBP content in the aqueous phase to be limited to a maximum of a few dozen mg/litre.
- Systematic monitoring of the absence of significant quantities of TBP in the different flows arriving in the evaporators of the units referred to, especially for the few flows which are not subject to washing with diluent.
- When aqueous solutions are transferred to the evaporators, the supply vessels are not completely emptied in order to avoid transferring any TBP which may be floating on the solutions.
- Before being received in distillation treatment units, organic effluents are systematically treated with carbonate and soda and washed with water in the "solvent treatments" of the different extraction cycles, which ensures a very low nitrate content in these effluents (a maximum of a few dozen mg/litre).
- To limit the temperature well below 135°C in normal operation inside "thermosyphon" evaporators (evaporators in intercycle concentration units, acid recovery units and oxalic mother liquor treatment units), the temperature of the coolant fluid is kept below that value (the temperatures of heating steam circulating in the boiler and the thermosyphon are around 130°C and 110°C respectively) and the heating loop is fitted both with a pressure regulator with a high pressure warning and a temperature regulation device with a high temperature warning which, when reached, cuts off the unit's steam supply. This temperature threshold (generally set at between 145°C and 150°C) allows a temperature below 135°C to be guaranteed anywhere in the evaporator. Finally, the vaporiser is protected by two valves whose loading limits any pressure increase in the cooling circuit and consequently limits the steam temperature.

For evaporators used in fission product concentration units (boiler type evaporators), the design of the cooling circuit in these units (double heating jacket) ensures that in normal operation the temperature throughout the liquid content remains below the temperature required to trigger the reaction. A complementary study confirmed, through simulation of the temperature of the internal

³ The first extraction cycle is composed of a stage of co-extraction of uranium and plutonium, followed by a phase of selective disextraction of plutonium (partitioning) then by a phase of disextraction of uranium before treatment of the spent solvent.

wall of this type of equipment, that the maximum temperature reached at the bottom of the boiler remained well below 135°C.

Finally, for evaporators in organic effluent treatment units (liquid film evaporators), the cooling circuit is fitted with pressure and temperature regulators with high pressure and temperature warning devices, and in addition the operator is warned of any excessively high temperature of the "residue" in the evaporator. The solvent temperature is also monitored when it leaves the evaporator, with a high temperature warning. These measures guarantee that a temperature of 135°C is not exceeded in these units.

These safety measures were assessed by the IRSN, specifically in degraded situations, when the different French reprocessing plants were commissioned.

Operating feedback from these plants has not revealed any evidence of incidents related to TBP/nitrate reactions.

These risks will be reviewed during the next safety reviews of these plants, taking particular account of the evolution of the characteristics of the fuel to be treated (risk of increased solvent degradation, etc).

References

W.W. Schulz and J.D. Navratil (1984), *Science and Technology of Tributyl Phosphate*, Vol.I, CRC Press

N.J. James and G.T. Sheppard, *Red Oil hazards in nuclear fuel reprocessing*, Nuclear Engineering and Design 130 (1991) 59-69

P.L. Gordon, C. O'Dell and J.G. Watkin, *Synthesis and energetic content of red oil*, Journal of Hazardous Materials 39 (1994) 87-105

V.N. Usachev and G.S. Markov, *Incidents caused by red oil phenomena at semi-scale and industrial radiochemical units*, Radiochemistry, Vol. 45, No. 1, 2003, pp. 1-8