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INFORMATION ABOUT THE ACCIDENT OCCURED NEAR RAPSODIE (1994, March 31th) *

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On March 31st, 1994, during the cleaning of the residual sodium contained in a tank located in a hall outside the containment building of the RAPSODIE reactor an explosion occured. One member of the CEA staff was killed and four people were wounded.
A commission of inquiry chaired by the CEA General Inspector for Nuclear Safety was set up by the "Administrateur Général" of the CEA the day following the accident. This Commission delivered its first conclusions in July 1994.
The sodium present in the tank in which the accident occurred comes from the primary cooling circuit of Rapsodie. After the final shutdown of the reactor, in 1982, all 37 metric tons of primary sodium were drained in 1985, then filtered to be purified from most of their radioactive contamination ; the 137 cesium activity, for instance, was reduced to about one hundredth of its original value.
After these operations, this sodium was stored for eight years in the tank, out of which it was syphoned in the second half of 1993 to be transformed into sodium hydroxide at the Desora facility. This facility, located inside the containment building of the reactor, had been especially designed for that purpose. When the tank was drained, there remained at the bottom, a residual sodium quantity.
Before dismantling, the tank had to be cleaned in order to remove this residual sodium. The process selected to perform this clean up operation, already implemented several times and notably in 1986 in a tank of similar geometry, consisted of progressively introducing in the tank a heavy alcohol, called ethyl-carbitol (CH_3-CH_2- O - $(CH_2)_2$ - O -(CH_2) - OH), while monitoring the reaction through temperature, pressure, hydrogen and oxygen measurements.
In its first conclusion the inquiry commission considered that the major cause of the accident was due to the formation of an heterogeneous physical-chemical environment, complex and multiphasic made up of three basic components (alcohol, alcolate, sodium). This environment developped after a cooling during several days due to a halt of alcohol injection, followed by an external electrical heating complemented by the local heat produced by the reaction themselves after resuming alcohol injection during the next last two days before the accident.
This environment turned out to be particularly favorable to the development of thermal decomposition reaction and/or catalytic exothermal reactions. Large quantities of gases (including hydrogen and light hydrocarbon compounds) were thus produced. Shortly after the last alcohol injection on March 31st, the phenomenum run out of control, leading to a sudden rupture of the overpressurised tank, then to the explosion of the gases mixture blown out in the hall.
The state of available knowledge did not allow the loss of control over such chemical reactions to be predicted or anticipated ; chemical reactions whose exact nature had not yet been determined. Consequently the Commission proposed a programme of detailed local investigations and a programme of complementary studies and analyses which involved basic knowledge of chemical reactions and chemical analyses of the reaction residues and

metallurgical, mechanical and thermal analyses and analyses linked to the human factor. Also the Commision proposed a programme of global chemical experiments in order to understand the integral phenomena.
Laboratories of the CEA, the chemical industry, the university and the CNRS were involved in carrying out this programme.
Consequently and in conformance with the commission of inquiry recommandantions :
- a project manager was appointed to carry out complementary studies,
- washing of sodium pools using alcohol will no longer be authorized as long as the studies and complementary appraisals have not been completed - an increased vigilance will be included in the design of the capacities containing dangerous products in order to facilitate future dismantling. Further vigilance will be required regarding the use of solvents and derived products, and regarding the presence after the final shutdown of a facility of a significant team having an excellent hnowledge of this facility.

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The first information on this accident was given at the meeting of May 1995.
It should be recalled that the accident took place in a basement next to the leaktight containment building of the reactor, at the end of dismantling operations. An explosion occurred during the destruction of 100 to 150 kg of sodium that remained at the bottom of a 55 m^3 tank. This destruction was performed by successive introductions of 50 l of ethylcarbitol. A member of the CEA team was killed and four other people were injured.
In addition to the administrative and judicial inquiries, the CEA set up an internal Inquiry Commission on July 94.
The latter concluded on :
⇨ The pneumatic explosion of the tank following unknown chemical reactions that occurred in the heterogeneous and multi-phase physico-chemical mixture that had formed during the washing operations, that had been suspended for several days, and during the heating of the system ;
⇨ The need to decree : design rules for equipment in order to facilitate its dismantling, organization principles in order to preserve the memory of the risks in the facility, and procedures for implementing dangerous products ;
⇨ The suspension of the ethylcarbitol cleaning technique ;
⇨ The need to pursue investigations in order to understand what happened and, if possible, to draw up principles to be respected in the future.
The investigation programmes were performed as defined, and provided the first results summarized below :
⇨ The accident area was cleared and the information gathered confirmed that there was pneumatic explosion of the tank, with a release of 200 MJ of energy (that is to say the equivalent of about fifty kilograms of TNT) ;
⇨ The chemical reactions and the fireball corresponding to the ignition of the gases released into the air did not constitute a significant energetic input ;
⇨ Metallurgical analyses, althrough not yet completed, have permitted the tearing lines in the tank's metal plate to be located and their origin situated ;
⇨ The chemical analyses focussed on :

- Analysing samples taken just after accident in the residue, and from the venting and ventilation circuits ;
- Attempting to identify the reactions that may have occurred ;
- Identifying and quantifying the gases produced when ethylcarbitol, ethylcarbitolate, a mixture of these two products, or a mixture of the products with the decomposition products generated by the various reactions, is heated. The abundant production of hydrogen was confirmed, in addition to the hydrogen expected from the reaction of the ethylcarbitol to the sodium, besides concentrations of carbon, methane, and carbon dioxide that increase when the temperature increases ;
- Defining the energies released as a function of overheating conditions. As long as the temperature remains below 220 or 230° C, exothermic reactions are slow, beyond this temperature, temperature increases of several hundred degrees in very short periods of time were measured ;
- Identifying the residues produced as a function of the temperature. These residues are of variable aspect and consistency, depending on the temperatures reached. They contain numerous, not yet identified intermediate products (up to 50 % for reaction temperatures ranging from 220 to 390°C), oxalate, carbonate, and amorphous carbon in varying proportions.

It was demonstred that isothermal exposures of ethylcarbitol/ethylcarbitolate blendings between 210 and 230°C can lead to exothermic reactions with an incubation time that increases as the temperature decreases. It was also recorded that some reactions could occur at room temperatures.

Future tests are in progress, focussed in particular on :

⇨The initiating cause of the runaway chemical reactions,

⇨The catalytic reactions that may occur.

Although these results confirm the initial conclusions of the internal Inquiry Commission, it has been shown that the chemical reactions at the origin of the accident are numerous and complex. They had not been explicitly described before 1994 and even today not all have been clearly defined. The conditions and causes of the runaway reactions that may occur even starting at ambient temperature, have to be specified.

The follow-up of the programme should provide results that will enable these phenomena to be quantified and thus clarify the feedback from this accident and the knowledge acquired since that time.

One should, however, particularly stress the need to maintain the suspension of the implementation of ethylcarbitol cleaning until definite conclusions have been drawn from both the analyses now in progress and future studies.