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EVALUATION OF BITUMINIZED WASTE REACTIVITY

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Although very few incidents have to be deplored all over the world in radioactive waste bituminization process, the bitumen inflammation risk has to be brought under control. In order to prevent such a risk, a zero thermal reactivity has been searched up to now to authorize an operationaly waste embedding. Elsewhere a model has been developed to predict the thermal behaviour of a drum during the cooling phase in order to precise how reasonable could be a non nul reactivity. One of the necessary input data is the evolution of the thermal power versus temperature. This document describes the experimental method proposed by the CEA to the plant operators to measure the potential reactivity of a waste destined to be conditioned in bitumen. Microcalorimetry has proved to be the most efficient technique. The application of this procedure is in progress at Marcoule Cogema plant and Saclay CEA center before all set up of bituminization operation.

INTRODUCTION

Bituminization process has been used in several countries for conditioning Low and Medium Activity (LMA) radioactive waste. This is an old tested process where is still implemented in some of them, in particular in France for the immobilization of coprecipitation slurries and evaporation concentrates resulting from effluents decontamination.

The process consists in mixing bitumen matrix with inactive soluble and unsoluble salts produced by radionuclides insolubilization or issued from neutralization of acidic effluents. The chemical composition of the salts precipitated in the slurries depends on the used reagents. Mixing is performed at a sufficient temperature to allow flowing of the resulting mixture in metallic containers. Mixing and heating occur simultaneously in Werner extruder (COGEMA La Hague, Marcoule) or thin film type Luwa machine (CEA Saclay). The filling temperature varies between 125 and 160°C according to waste composition and bitumen grade. Drums are generally filled up with successive layers of salts/bitumen mixture.

If no incidents have occured at La Hague COGEMA plant since 1989 and at Marcoule plant since 1966, a few thermal incidents have to be deplored in production of bituminized waste all over the world. As far as nuclear safety is concerned, this risk has to be brought under control. Then the CEA has been involved for many years in evaluating the thermal reactivity of bituminized waste and its consequences on bitumen process.

A first approach consists in the definition of a working scope in order to precise the admissible range of main parameters (flowing temperature, reagents dose, ...) in regards to the inquired nul reactivity.

However treated effluents are able to include impurities that may have incidence on thermal behaviour of bituminized waste. Then the characterization of the potential reactivity appears as further precautionary measure. Consequently the CEA has developed studies on this aspect. These studies aim to supply the plants operators with a methodology able to identify a hazardous mixing and to guarantee the safety of the process to authorities.

EVALUATION OF BITUMEN INFLAMMATION RISK : SELECTED APPROACH

Exothermal reactions between salts and bitumen can be induced during the mixing phase. They may thus produce an additional heat emission that the material must be able to release in order to avoid a potentially incidental pattern.

Both main mechanisms responsible for heat evacuation from bituminized waste are :
- thermal conduction,
- convection induced by a difference of temperature between the core and the surface of the drums. This last phenomenon is essential to insure safety of the process when salts bring some reactivity.

Many characteristics of bituminized waste concur towards inflammation risks :
- low thermal conductivity of bitumen matrix,

- high viscosity (depending upon dry mineral extract content, mixing temperature, ..). If viscosity is very high, the conduction may become the predominant heat release mechanism,
- exothermicity of redox reactions (function of waste nature).

If the pouring temperature is not well-controlled, a risk exists to fall over an incidental scenario.

The risk of bitumen inflammation generally increases with the filling of the drum ; therefore the highest one occurs *after* the filling-up. In some cases, when reactivity is very important, risks may occur before the end of drum filling up. The control of these risks requires an evaluation of heat release ability compared to the heat generated by reactivity.

The selected approach is based on the modelling of phenomena responsible respectively for heat production and heat evacuation. This model is detailed in the lecture of P.Mercier. It describes the thermal behaviour of a drum during the cooling phase and thus makes possible the prediction of mixing safety for a given slurry/bitumen couple.

A sensitivity study concludes that main parameters for calculations are :

- the thermal power brought by exothermal reactions,
- rheological properties of salts/bitumen mixtures.

Both parameters are input data of the developed model and have to be lab-scale measured before every bituminization operation.

This paper deals with the experimental measure of the thermal reactivity that has been specifically established.

Considering the complexity of slurries chemical composition, the method does not intend to distinguish each possible redox reaction but is based on a global reactivity evaluation of the BWP. Microcalorimetry has proved to be the most efficient technique to characterize this potential global reactivity .

EXPERIMENTAL METHODOLOGY FOR REACTIVITY DETERMINATION

Preparation of the Bitumen Waste Products (BWP)

BWP destined to reactivity measurement are elaborated in a specific way. In order to avoid the consumption of all or part of the thermal potential reactivity during their elaboration, slurries are filtered, dried at low temperature (about 60°C) and grinded before to be incorporated in bitumen at low temperature (about 75°C). Preliminary studies showed that no reactivity has been detected at temperature lower than 100°C. The bitumen ratio is in accordance with the industrial one.

Acquisition of the calorimetric signal

Measurements of thermal flux are performed with a SETARAM C80 microcalorimeter.
First tests were performed in *dynamical modus* : samples were heated from room temperature to 300°C at 0.5 °C/min. This procedure is adapted to display directly the temperature of the beginning exothermicity. But it does not allow to measure precisely the upper limit of the released thermal power at a given temperature. This conclusion leads to work in *isothermal modus*.

In this case, for each BWP, the power signal is measured during different tests performed at temperature around the pouring one (120 – 140 – 160 – 180 – 200°C range).
The heating of samples up to the isotherm temperature is performed at 0,5°C/min, the recommended speedby SETARAM manufacturer considering the system inertia. During this step, the thermal equilibrium between the « measurement » and the « reference » cells is not well established. The thermal power signal obtained is not rigorously analyzable related to the precision in demand (about 1 mW/g).

During the isothermal phase, the calorimetric unit thermally stabilizes : temperatures in both cells are identical and all exothermal (or endothermal) reactions occuring in the measurement cell produce a signal gap above (respectively below) the baseline. The decreasing form of the signal expresses the depletion of one or more reactions occuring inside the BWP versus time. Term of the stage depends on the temperature : it has to insure a baseline return, that guarantees the total consumption of the BWP thermal reactivity.

The measurement is realised in two steps :

- firstly, the measurement cell contains the sample and the reference cell contains an equivalent mass of inert alumina. This compensation allows to limit the imbalance between both measuring cells. The raw signal thus obtained at each temperature is correlated to the thermal flux difference between both ways of measure ;
- secondly, the measurement cell contains a synthetic bitumen/alumina product (elaborated in the same conditions of temperature and bitumen/salt ratio as the sample) and the reference cell contains an equivalent mass of inert alumina.

  This last signal is substracted from the first one. Advantages of this procedure are :
- to cast off the signal due to oxidation of bitumen by oxygen trapped in the cell,
- to avoid the endothermal signal resulting from the heating phase,
- to take into account the gap between both ways of measure depending upon the asymmetry of measure and reference ways.

APPLICATION OF THE METHOD TO SYNTHETIC BITUMEN WASTE PRODUCT

This method has been applied to inactive synthetic BWP in order to appreciate the contribution to the reactivity of each component of the slurry with regards to the reference composition.

Primary waste was an inactive acidic effluent. A simulated coprecipitation treatment was applied, including precipitates formation from reaction of :
- baryum nitrate in sulfuric media,
- potassium ferrocyanide and nickel sulfate,
- iron and cupper sulfates at basic pH.

Slurries containing respectively one, two and all of these three reagents were elaborated and each respective reactivity was determined by the microcalorimetric method. An example of signal obtained in the case of the slurry including all precipitates is given in Figure 1.

The evolution of maximal thermal power versus temperature is plotted for all samples on Figure 2.

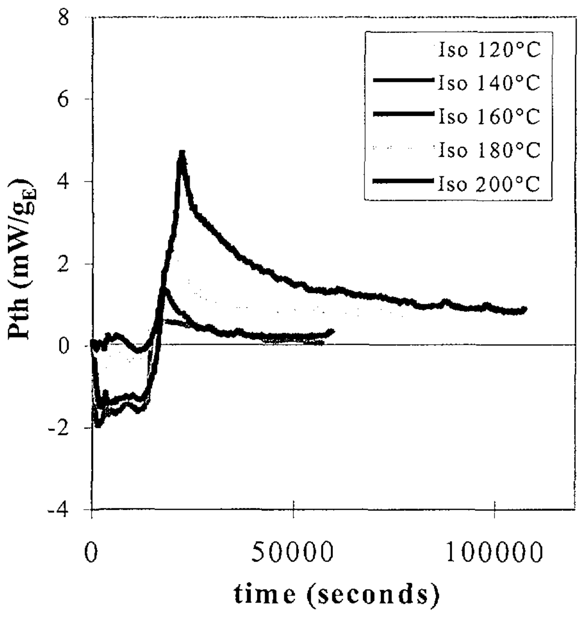

Figure 1 : Microcalorimetric analysis of reference sample – Typical curve

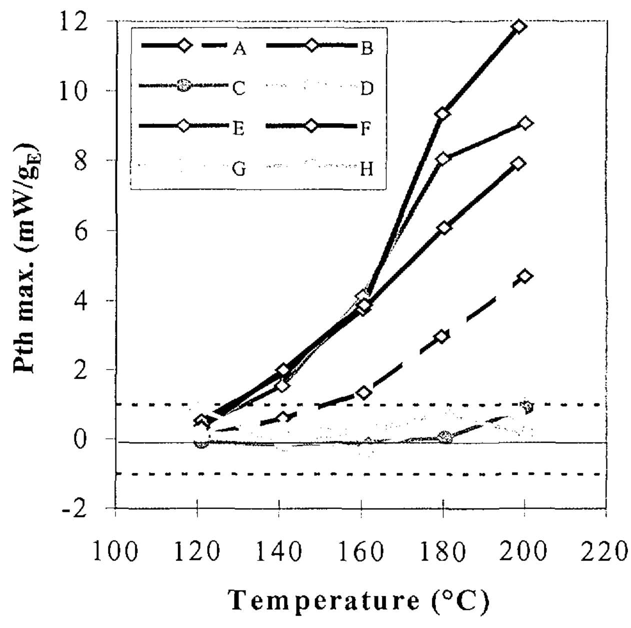

Figure 2 : Evolution of maximal thermal power versus temperature

A : reference, **B** : $Na_2SO_4/Ba(NO_3)_2$, $FeSO_4/CuSO_4$

C : $Na_2SO_4/Ba(NO_3)_2$, PPFNi **D** : $Na_2SO_4/Ba(NO_3)_2$

E : $FeSO_4/CuSO_4$, PPFNi **F** : $FeSO_4/CuSO_4$

G : PPFNi **H** : without reagents

No significative (< 1 mW/g) reactivity is noted for the lowest temperature (120°C) for all samples. From 140°C, two types of behaviour are noticed :

- a higher exothermicity than the reference one for samples that initially included iron and cupper sulfates. This reactivity increases with temperature.
- the lack of significant exothermicity for BWP that does not initially contain sulfates reagents.

These measurementss prove the significant effect of iron/cupper sulfate content on BWP reactivity and the importance of the pouring temperature's control for the safety of the process.

Further studies need to link these measurements to the probability that inflammation risk could occur.

CONCLUSION

An experimental method has been developed by the CEA in order to evaluate the thermal reactivity of slurries destined to be conditioned in bitumen . This method is based on microcalorimetric measurements. It allows to determine the evolution of the maximal thermal power versus temperature and thus to compare different slurries between themselves.

On this point of view, a specific study shows that the introduction of iron and cupper sulfates as reagents for coprecipitation tends to increase the reactivity of a given waste.

This procedure has been developed for nuclear applications : its application is in progress at Marcoule COGEMA plant and Saclay CEA center as an acceptability criteria before all bituminization operations.

Nevertheless, one must keep in mind that this reactivity is only one of the entry data of the modelling destined to predict the incident risks of bitumen drums elaboration. In fact, main thermal energy released from a bitumen drum is due to convection phenomenon. Then it is strongly dependent on rheological properties of the material that have to be separately determined.