Chemical Reactivity of Nitrates and Nitrites Towards TBP and Potassium Nickel Ferrocyanide between 30 and 300°C

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ABSTRACT

Since the late sixties, bitumen has been widely used by the nuclear industry as a matrix for the immobilization of low- and intermediate level radioactive waste originating mainly from the nuclear activities: precipitation or evaporator concentrates, ion exchange resins, incinerator ashes, and filter materials.

Depending on bitumen and operating conditions, bitumization of radioactive waste can be operated between 130 and 180°C, so chemical reaction can be induced with nitrate or nitrite towards elements contained in waste (TPB, potassium nickel ferrocyanide and cobalt compound…) and bitumen. These reactions are mainly exothermic this is the reason why the enthalpy reaction and their temperature of initiation have to be determined independently of their concentration in waste.

In this work, we have studied by Calvet Calorimetry at 0.1 °C/min heating rates, the behaviour of chemical elements especially oxydo-reduction couples that can react at a temperature range 100-300°C (Nitrate/PPFeNi, Nitrite/PPFeNi, Nitrate/TBP, Nitrite/TBP, Nitrate/bitumen and Nitrite/bitumen).

The initial temperature reaction of nitrates or nitrites towards potassium nickel ferrocyanide (PPFeNi) has been studied and is equal respectively to 225°C and 175°C. Because of the large scale temperature reaction of nitrate and PPFeNi, enthalpy reaction can not be calculated, although enthalpy reaction of nitrite and PPFeNi is equal to 270 kJ/mol of nitrite.

Sodium Nitrate and TBP behaviour has been investigated, and an exothermic reaction at 135°C until 250°C is evidenced. The exothermic energy reaction is a function of TBP concentration and the enthalpy reaction has been determined.

INTRODUCTION

Since the late sixties, bitumen has been widely used by the nuclear industry as a matrix for the immobilization of low- and intermediate level radioactive waste originating mainly from the nuclear activities: precipitation or evaporator concentrates, ion exchange resins, incinerator ashes, and filter materials.

Depending on bitumen and operating conditions, bitumization of radioactive waste can be operated between 130 and 180°C, so chemical reaction can be induced with nitrate or nitrite towards elements contained in waste (TPB, potassium nickel ferrocyanide and cobalt compound…) and bitumen. These reactions are mainly exothermic this is the reason why the enthalpy reaction and their temperature of initiation have been determined independently of their concentration in waste.

In the frame of the storage of organic-bearing radioactive high level waste at the US Department of Energy's Hanford Site, many studies have been performed on the thermal reactivity of organic-bearing radioactive waste such as organic complexants (EDTA) [1] , Tri-butyl phosphate (TBP) [2] and alkali nickel ferrocyanides [3,4]

The objective of the present study is to figure out the thermal reactivity by using calorimetry methods between nitrate/nitrite mixtures and selected elements contained in waste (TPB, potassium nickel ferrocyanide).

EXPERIMENTAL

Differential Scanning Calorimetry

In order to determine the reaction of nitrate and nitrite with TPB and potassium nickel ferrocyanide, we have used a thermal analyzer 3D-sensor calorimetric (C80 SETARAM model). The C80 calorimeter used in this study belongs to the CALVET calorimeters family distinguished by their accurate and reproducible calorimetric measurements. It is adapted to temperature scanning calorimetry. The instrument was designed to study materials transformation over the temperature range from 30°C to 300°C. In this study, the samples were heated in the high-pressure sample vessel at a 0.1°C/min heating rate from 30°C to 300°C. The mass of the sample was about 0.5 g and an equivalent mass of alumina was loaded into the reference vessel. The samples are loaded in high-pressure vessel with nitrogen, prepared in a glove box under nitrogen.
During experiment, the heat flow is measured from 30°C to 300°C, and then heat flow is corrected with a heat flow obtained with alumina in sample and reference vessel. This heat flow correction has to be made because of the deviation of heat flow calorimeter with temperatures.

Preparation of materials

The scanning calorimetry on nitrate or nitrite mixtures with TBP and potassium nickel ferrocyanide was performed as solid materials. $NaNO_3$, $NaNO_2$ and TBP were purchased from commercial chemical supply company.
Potassium nickel ferrocyanide compound was prepared by aqueous method by dissolving $K_4Fe(CN)_6,3H_2O$ (0.0858 M) in aqueous solution and adding $NiSO_4,7H_2O$ (0.103 M), the solution was agitated for 2 hours at room temperature. The solids were dried at 50°C under nitrogen atmosphere.

RESULTS AND DISCUSSIONS

Reactions of TBP and PPFeNi with sodium nitrate and sodium nitrite were studied between 30 and 300°C. The objectives were to determine the reaction temperature range and the enthalpy reaction.

Thermal behavior of TBP with sodium nitrate and sodium nitrite

Previous studies have pointed out the thermal impact of TBP with thorium nitrate and nitric acid, continuous mass spectrometric analysis of the gaseous reaction products allowed identification of the reactions occurring in these mixtures [2,5].
In the literature, an extensive study [6] has been performed on thermal behaviour of sodium nitrate and sodium nitrite with organic complexants (EDTA, HEDTA and citrate) used in Purex operations. The thermoanalytical studies indicate that dry organic-bearing wastes containing the organic sodium citrate or Na_4EDTA or Na_3HEDTA and sodium nitrate and nitrite present an exothermic reaction at 180°C.
In our work, we have studied the influence of TBP/sodium nitrate ratio by thermal analysis. On Figure 1 is reported various thermal analysis at various TBP/$NaNO_3$ ratio. This figure shows an exothermic reaction over the temperature range, 150°C to 250°C. The initial temperature reaction is equal to 160°C, and is independent on the TBP/$NaNO_3$ ratio.
The heat flow increases with the TBP/$NaNO_3$ ratio, these heat flows are a linear function of TBP concentration; the enthalpy reaction can be calculated in the temperature range 150°C to 210°C and is equal to -550 kJ/mol of TBP. G.S. Barney [2] has determined the TBP enthalpy decomposition at temperature range 112°C to 268°C and has obtained -60.6 kJ/mol of TBP. Consequently, the exothermic reaction observed with TBP/$NaNO_3$ can really be attributed to the reactivity of TPB and $NaNO_3$.

Radioactive waste can contain small amount of sodium nitrite and can react with TBP at high temperature. The thermal behavior of sodium nitrite and TBP mixtures with various ratio is reported on Figure 2. It appears that exothermic reactions between TPB and sodium nitrite begin at 120°C until 270°C, the initial exothermic temperature is independent on the mixture composition and is equal to 120°C.
The heat flow increases with the TBP/$NaNO_2$ ratio, these heat flows are linear with the TBP increasing temperature. The enthalpy reactions can be calculated in the temperature range 120°C to 190°C and 120°C to 270°C and are equal respectively to -306 kJ/mol of TBP and -1202 kJ/mol of TBP.

Comparison of the thermal behavior of TBP and sodium nitrate with TBP and sodium nitrite mixtures shows that the initial exothermic temperature in lower with sodium nitrite (120°C) than with sodium nitrate (150°C) and the enthalpy reaction of TBP with sodium nitrate is slightly more important than with sodium nitrite for a temperature range of 60-70°C.

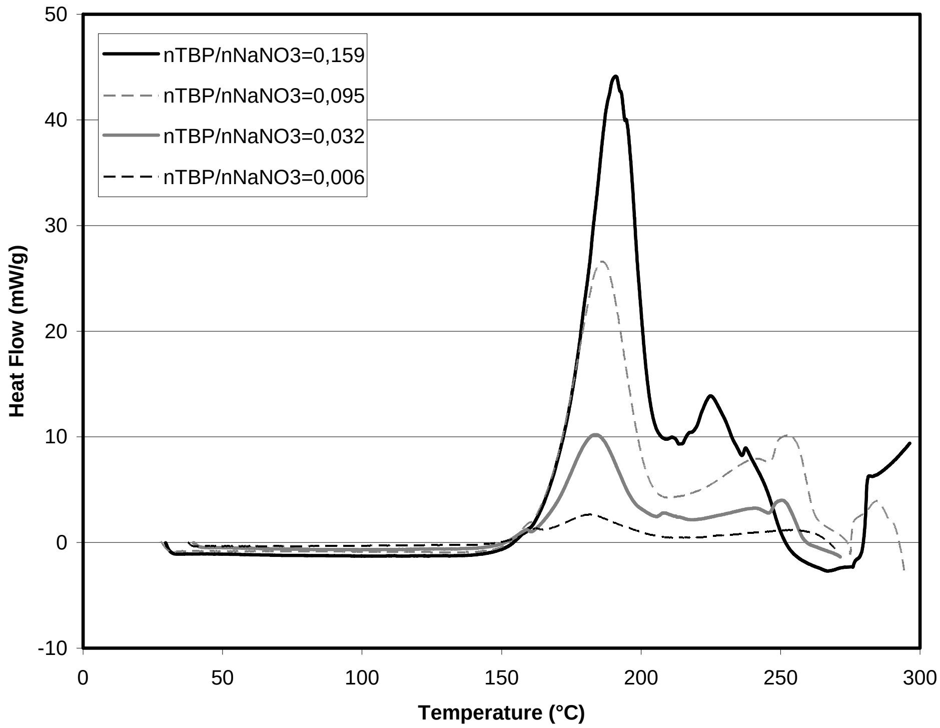

Fig.1: Thermal analysis of various TBP/sodium nitrate ratio, heating rate: 0.1°C/mn, atmosphere: nitrogen

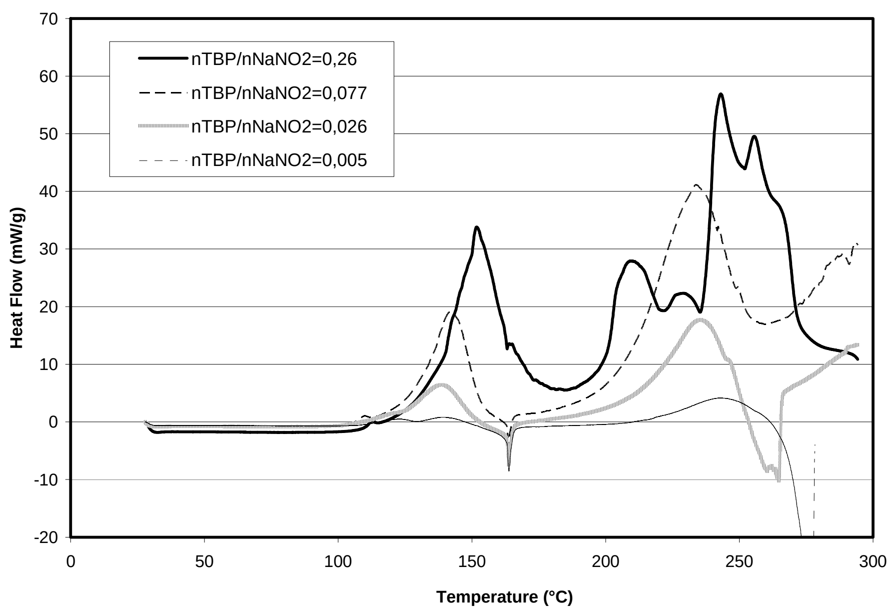

Fig.2: Thermal analysis of various TBP/sodium nitrite ratio, heating rate: 0.1°C/mn, atmosphere: nitrogen

Thermal behavior of precipitated potassium nickel ferrocyanide (PPFeNi) with sodium nitrate and sodium nitrite

Pacific National Laboratory (USA) has performed an important experimental program on the effects of temperature on the oxidation reaction between synthetic nickel cesium ferrocyanide (PPFeNi) with nitrates and nitrites in the frame of the Hanford tanks [1, 3, 4, 7]. The major experimental method was the thermal explosivity studies (TTX test) used in the explosion industry. Differential scanning calorimetry measurements have been also completed to determine temperature reaction but it appears that the position of exothermic reaction depends on the heating rate (1°C/min to 10°C/min). In these studies, the heating rate was equal to 5°C/min. The objective of these studies was to calculate the critical temperature based on time to explosion measurements with various conditions. In our work, we have focused to estimate the initial exothermic temperature of exothermic reaction and to determine the enthalpy reaction with a binary PPFeNi/$NaNO_2$ at a slow heating rate (0.1°C/min).
A scanning calorimetry with PPFeNi/$NaNO_3$ and PPFeNi/$NaNO_2$ is reported on Figure 3 to evaluate the thermal behavior of these binary. The exothermic reactions begin over 150°C for $NaNO_2$/PPFeNi and 200°C for $NaNO_3$/PPFeNi. For $NaNO_3$/PPFeNi, the exothermic reactions occur at an important temperature range (over 300°C), therefore enthalpy reaction can not be calculated.
The thermal behaviors of PPFe/NaNO2 mixtures at various ratios have been reported on Figure 4. The heat flows increase with the $NaNO_2$/PPFeNi ratio, the onset temperatures of various $NaNO_2$/PPFeNi ratios evolve with composition, however the onset temperatures are between 150°C and 200°C.
A thermal study on PPFeNi with $NaNO_3$ and $NaNO_2$ has been performed by differential scanning calorimetry at 5°C/min [3] and showed that for a pure nitrate and/or nitrite, the minimum observed reaction temperature is 230°C. The deviation with our value is due to the heating rate 0.1°C/min used in our work, the exothermal reaction position shifted toward lower temperature as the heating rate decreased.

The evolution of heat flow with $NaNO_2$ concentration permits us to calculate the enthalpy reaction and is equal to -270 kJ/mol of $NaNO_2$.
The mole ratio of $NaNO_2$ to PPFeNi in reaction between 160°C and 270°C has been calculated by using an energy- $nNaNO_2$/nPPFeNi plot. A maximum is obtained for $NaNO_2$ and PPFeNi ratio 10:1. So, the enthalpy reaction between PPFeNi and $NaNO_2$ is assumed equal to -2700 kJ and the potential reaction (Eq.1) can be written as follows:

$K_2NiFe(CN)_6$+10$NaN0_2$ =FeO, NiO, CO_2, N_2, NaK hydroxides or NaK carbonates or NaK oxides (Eq.1)

The products of the reaction are unknown so a various hydroxides, carbonates or oxides can be produced.

A thermodynamics study has been performed by L.L. Burger *et al.* [3] on potential reaction of $NaNO_2$ with cesium ferrocyanide ($Cs_2NiFe(CN)_6$) and the enthalpy reaction is ranging from -1705 kJ (Na, Cs oxides products) to -2925 kJ (Na, Cs hydroxides products). Our value is in the same order of these two thermodynamic determinations.

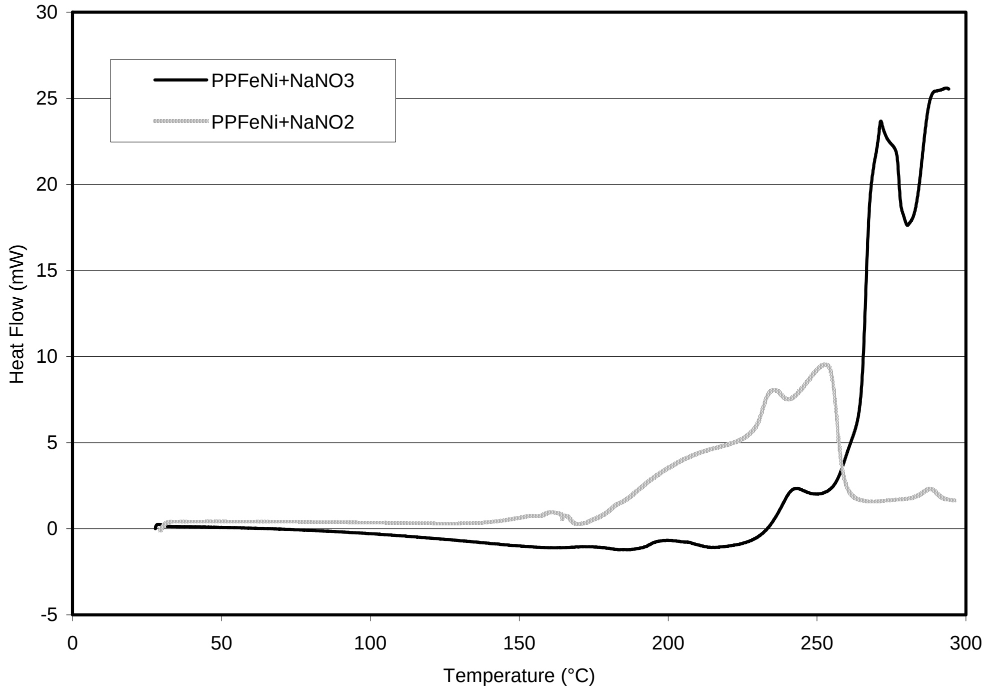

Fig. 3: Thermal analysis of PPFeNi/$NaNO_3$ and PPFeNi/$NaNO_2$ mixtures, heating rate: 0.1°C/mn, atmosphere: nitrogen

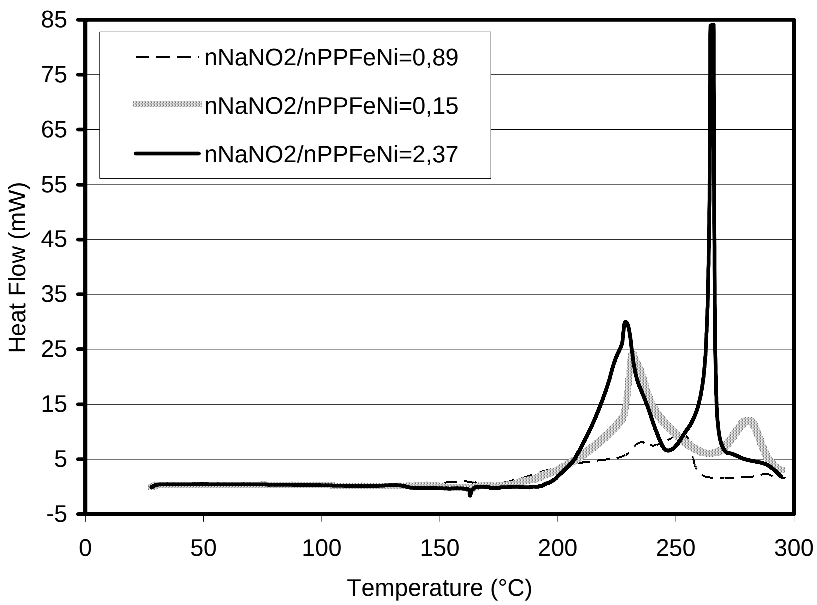

Fig. 4: Thermal analysis of various sodium nitrite/PPFeNi ratio, heating rate: 0.1°C/mn, atmosphere: nitrogen

CONCLUSIONS

The goal of this work was to investigate the thermal behavior of binary mixtures of TBP with sodium nitrate or nitrite and potassium nickel ferrocyanide with sodium nitrate or nitrite by using scanning calorimetry method.

The thermal analysis studies show that the exothermic reactions of TBP with sodium nitrite and nitrate begin respectively at 120°C and 150°C. The enthalpy reactions have been calculated and are reported below:

- TBP/$NaNO_3$: -550 kJ/mol of TBP (temperature range 150°C to 210°C)
- TBP/$NaNO_2$: -306 kJ/mol of TBP (temperature range 100°C to 180°C)
- $NaNO_2$/PPFeNi: -270 kJ/mol of $NaNO_2$ (temperature range 160°C to 270°C)

The mole ration of $NaNO_2$ to PPFeNi in reaction between 160°C and 270°C has been calculated by using an energy- n$NaNO_2$/nPPFeNi plot. The mole ration of $NaNO_2$ to PPFeNi is equal to 10:1.

The calorimetry measurements show that exothermic reactions with TBP and PPFeNi are multistep reactions, and the reaction products have to be determined to understand the reaction mechanisms.

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