# EXPERIMENTAL AND SIMULATED STUDY OF A HYDROTHERMAL OXIDATION REACTOR : UNSTEADY REACTOR BEHAVIOUR AFTER A REACTOR STOP.

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**Abstract**

The scaling up of Hydrothermal oxidation (HOT) facility depends on the development of simulation tools. In this way, we propose a new approach to simulate the reactor thermal behaviour during a emergency stop of the unit. A numerical procedure of non stationary temperature profile simulation in the reactor is described in order to predict the reactor thermal behaviour. This new model is validated from experimental data obtained with a quasi-adiabatic reactor, which allow to follow the temperature profile evolution along the reactor during the HOT process. Performances of numerical procedure are tested with simulation of a real non stationary conditions: pump defect. The simulations give evolutions of temperature profiles of reactive mixture versus time and external wall temperature of reactor tube versus time. These simulations show that the HOT reactor thermal operation can be considered as stable and sure during a emergency pumps stop.

**Keywords**

Hydrothermal oxidation, unsteady simulation, thermal risks evaluation, scaling up.

## 1 - Introduction

The knowledge of the reactor thermal behaviour during transition phases as an emergency stop is very important for the development of the process in regard with the facility performances and the security (for example, to overcome irreversible reactor damages). But most of the simulation tools operate in steady state and models in non stationary phenomena are limited.
From this point of view, we propose a model which can simulate the reactor thermal behaviour in non stationary regime. This model is validated from data obtained with continuous pilot plant facility.
First, experimental results are presented. These results have been obtained by using a quasi-adiabatic reactor, developed at the ICMCB. This reactor allows to follow the temperature profiles along the reactor during the oxidation reaction. Then the experimental data will be used to validate the numerical procedure are presented.
Second, the numerical program which simulates the thermal behaviour of this reactor in stationary and non stationary regimes is described.
Third, simulation results are proposed in regard to the experimental tests. Simulations of a non-stationary situation are described: pump defect

## 2 - Experimental results

The quasi-adiabatic tubular reactor was developed at ICMCB in order to determine heat quantity produced by hydrothermal oxidation reactions of model molecules and industrial wastes [1]. This reactor is made of Inconel 718 tube of 2.4 mm inside diameter and 8.4 m length. It is equipped with 28 thermocouples (type K) distributed along the reactor. The tube is isolated with ceramic fiber and surrounded with a thermal shield. The thermal shield is constituted of a copper sheet surrounded with an electrical heating in order to reduce thermal loss. The reactor allows to obtain temperature profiles along the tube and inlet and outlet COD [2].
The experiments were performed at 25 MPa. The wastewaters were injected in the reactor at 400°C and the oxidant, hydrogen peroxide, was injected in the reactor at room temperature in order to avoid it's decomposition during the preheating. The hydrogen peroxide concentration of the oxidant feed solution was 166 g/l and the flow rate was adjusted from the waste flow rate and COD in order to bring $H_2O_2$ in the reactor in stoichiometry.
The reactor thermal behaviour was studied from a real industrial wastewater. The exact composition of this wastewater is not well known.
The operating conditions of the pilot facility (oxidant and waste mass flow rates 0.5 $kg.h^{-1}$ respectively). Inlet COD: 57800 $kg.m^{-3}$ and outlet COD: 0.02 $kg.m^{-3}$

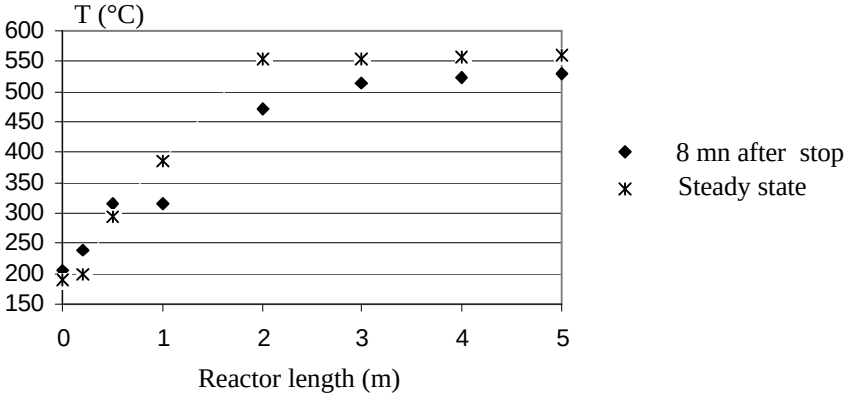


**Figure 1** : Evolution of the temperature profiles along the reactor in steady state and eight minutes after a facility stop

Figure 1 shows the temperature profiles obtained with the quasi-adiabatic reactor working in steady state and eight minutes after the facility stop. The maximum of temperature (572 °C) is located two meters after the reactor inlet.
These experimental tests put in prominent position that it is possible to follow the thermal evolution of HOT reactor from the quasi-adiabatic reactor developed at the ICMCB and show the process thermal stability in regard with the reactor during the facility stop.
These tests will be used to validate the model that we have developed.

**3 - Numerical simulation**

The reactor is tubular and the flow is turbulent, so we can neglected body forces effect and radial contributions. These considerations imply the use of a one-dimensional model for the study the reactive fluid and the metal and the insulated material requires the use of a two-dimensional model in order to tack into account the radial heat dissipation.
The numerical model requires simultaneous resolution of momentum, mass balance, energy and chemical specie conservation unsteady equations in the fluid and of the energy conservation equations in the metal and in the insulated material. So, the set of equations [3]:

*Flow equations (z = 0 to L)*

$$\frac{\partial r}{\partial t}+\frac{\partial}{\partial z}(r.u)=0 \qquad (1)$$

$$r.\frac{\partial u}{\partial t}+r.u.\frac{\partial u}{\partial z}=-\frac{\partial P}{\partial z}+\frac{4}{3}\frac{\partial}{\partial z}\left(m\frac{\partial u}{\partial z}\right) \qquad (2)$$

$$\frac{\partial C}{\partial t}+\frac{\partial u.C}{\partial z}=D.\frac{\partial^2 C}{\partial z^2}-k \qquad (3)$$

$$r.C_p.\frac{\partial T}{\partial t}+r.u.C_p.\frac{\partial T}{\partial z}+\frac{T}{r}\left(\frac{\partial r}{\partial T}\right)_P.\left[\frac{\partial P}{\partial t}+u.\frac{\partial P}{\partial z}\right]=\frac{\partial}{\partial z}\left(l\frac{\partial T}{\partial z}\right)^2-\Delta H.k+\dot{q}(z) \qquad (4)$$

*energy conservation in the metal ($r = R_1$ to $R_2$)*

$$r_m.C_{Pm}\frac{\partial T_m}{\partial t}=l_m\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T_m}{\partial r}\right)+\frac{\partial^2 T_m}{\partial z^2}\right] \qquad (5)$$

*energy conservation in the insulated material ($r = R_2$ to $R_3$)*

$$r_i.C_{Pi}\frac{\partial T_i}{\partial t}=l_i\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T_i}{\partial r}\right)+\frac{\partial^2 T_i}{\partial z^2}\right] \qquad (6)$$

It is necessary to add to this system, the radial continuity of heat flux between the fluid and the metal and between the metal and the insulated material.

With u the fluid velocity, P the static pressure, μ the turbulent dynamic viscosity, C the waste concentration in the fluid, k the waste reaction velocity, D the turbulent diffusion coefficient, ΔH the reaction heat, $\dot{q}(z)$ the volume heat exchanged with the reactor material, T the

temperature, Cp the specific heat, λ the thermal conductivity, $r$ the density, r is the radius, $R_1$ and $R_2$ are, respectively, the internal and external radius of the annular material, $R_3$ the external radius of the insulated material.
The functions without subscript are relative to the fluid properties. The subscripts m and i are relative to the metal and to the insulated material, respectively.

This part of the program allows to determine the steady state and the unsteady behaviours of the reactor. The different stationary profiles will be used as initial conditions in the non stationary simulations.

*Resolution :*

This system of six equations is solved simultaneously. This program permits to modulate the inlet mass flow rate ($\dot{m}$). The velocity, temperature and concentration profiles are estimated by using an integral method (Euler) with a constant time step and the spatial variations by using the finished difference method.

*Chemical reactions*:

According to the literature [4], the oxidation reaction kinetics, used in this program, are first order in regard with the waste and zero order in regard with the hydrogen peroxide. A numerical program [5] had been developed to allow the determination of reaction heat and kinetic parameters. This program calculates these properties by using experimental results and numerical simulations.

**V – numerical results and validation**

From a thermodynamic point of view, we have considered the fluid as pure water. ″The 1967 IFC Formulation for industrial use″ [6] was used to determine thermo-physical properties of pure water at 25 MPa.
The simulations, were performed in the same conditions as those of the experimental test (static pressure, inlet temperature, concentration and mass flow rate).

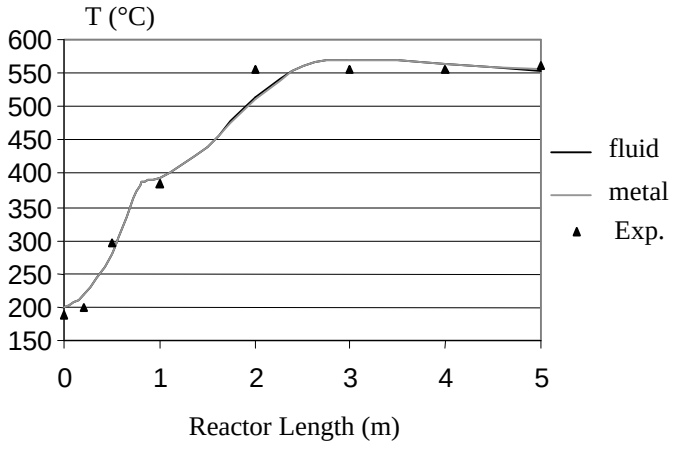


**Figure 2**: Experimental and simulated temperature profiles (reactive mixture and reactor tube). Steady state problem.

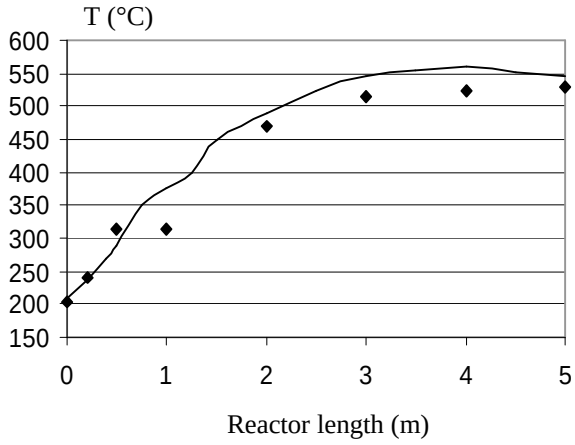


**Figure 3**: Experimental and simulated temperature profiles (reactive mixture and reactor tube) of the reactor 8 minutes after the pumps stop

In steady state, the simulated temperature profile along the reactor is closed to the experimental one (Figure 2).

We have tested our model in the case where we stop the high pressure pump (waste and oxidant). The comparison of the experimental and simulated temperature profiles along the reactor 8 minutes after the pumps stop is shown in Figure 3. The simulated temperature profile agrees with the experimental temperatures and similar to the external wall of metallic material. This last point is due to the characteristic time of heat transfer in the reactor tube alloy which is lower than one minute.
As shown in Figures 2 and 3, the good agreement between the experimental and simulated temperature profiles valids the developed numerical procedure.

The numerical model being validated, the simulation of the temperature profiles along the reactor during non-stationary regimes can be investigated. The simulation of this non-stationary condition is performed in regard with the reactor thermal behaviour (reactive mixture fluid and external wall of the reactor tube) at different times.

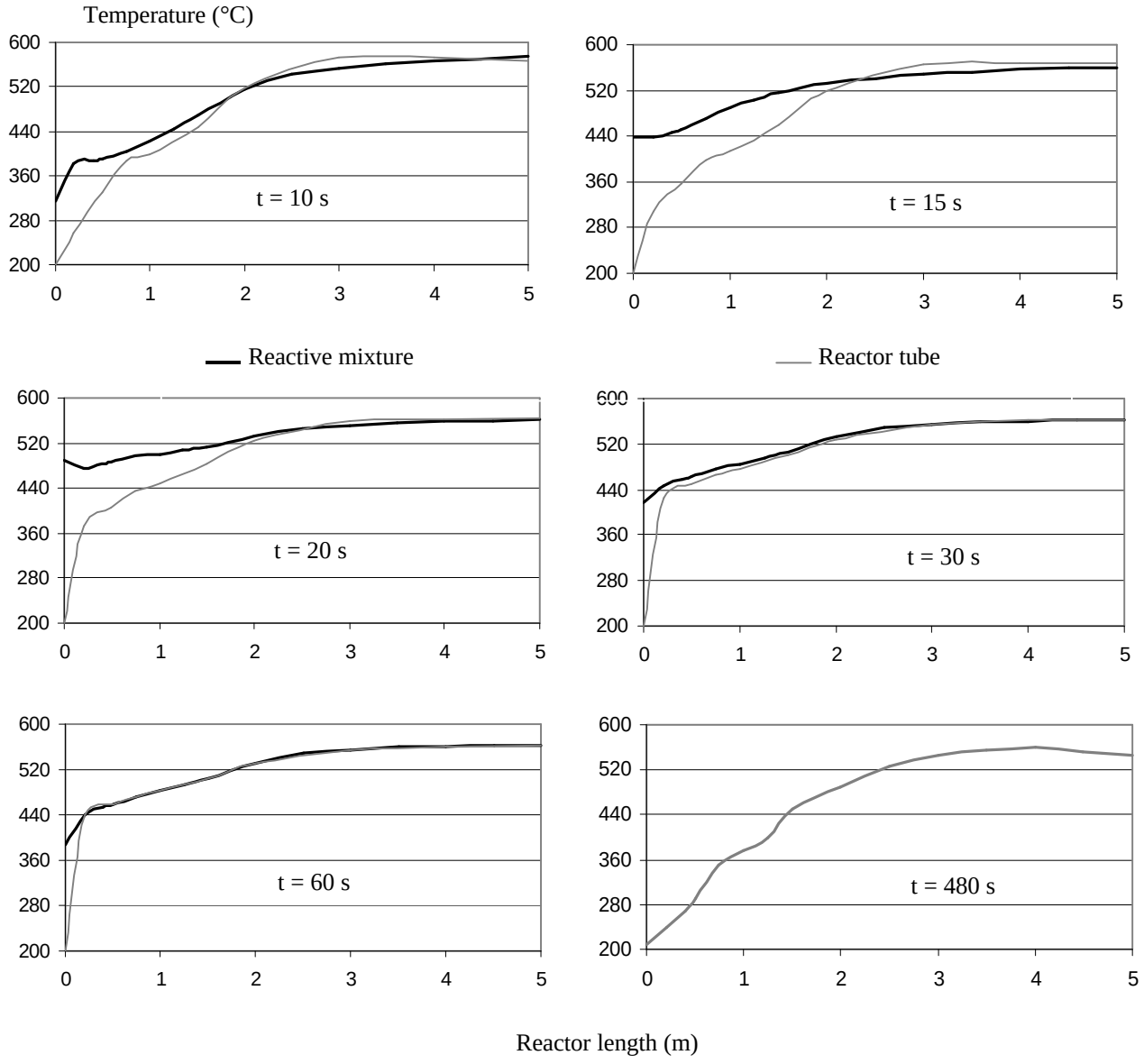


**Figure 4:** temperature profiles of reactive mixture (—) and wall reactor (—)versus time after pumps stop

The figure 4 presents the temperature profiles of the fluid and the metal during the first minute after the pumps stop. At $t < 0$, the reactor works in steady state. At $t = 0$, the injections of waste

and oxidant are stopped. The thermal equilibrium is obtained after several hours because the heat exchange between metal and the insulated material are very slow. It is significant to notice that there is a high difference of temperature between the reactive fluid and the reactor tube. This difference can be higher than 300 °C at the reactor inlet.
After the reactor stop, the reaction goes on in the reactor, especially where the waste and oxidant mass fractions are high level. The heat generated by the reaction can not be dissipated except by volumetric expansion because the heat quantity evacuated per time unity across the insulated material is poor.
In this study, in steady state, the conversion is complete and the higher temperature is around 570 °C. During the facility stop, the temperature in the reactor is always lower than 570 °C

## VII - Conclusion

Numerical procedure of simulation in non-stationary working of HOT reactor thermal behaviour has been described. The simulation allows to predict the temperature profiles of the fluid along the reactor and the reactor walls.

This model has been validated from experimental temperature profiles obtained with a quasi-adiabatic tubular reactor. Experimental temperature profiles has been measured for a real industrial waste and the evolution of the these profiles was followed during steady state functioning and pump stop. A good agreement between experimental and simulated temperature profiles along the reactor was obtained and the model is so validated.

The performances of the validated numerical procedure have been tested with the simulation of pump defect. The simulations give the evolution of the temperature profiles of the fluid and the reactor wall versus the time. These simulations show that the HOT reactor thermal operation can be considered as stable and sure during the reactor stop. They point out that the risks of reactor damage are limited and that the developed model is able to evaluate the dangers in regard with the reactor thermal behaviour.

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