

FLUID MIXING AND THE SAFE QUENCHING OF A RUNAWAY REACTION IN A STIRRED AUTOCLAVE

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The network-of-zones model has been used to analyse the mixing behaviour in 3D when a cold slug of quenchant material is injected into a batch of reactants. In this way, it is possible to make predictions of the conditions required for achieving a safe quench when a reaction is close to a runaway condition. Some illustrations are presented for styrene polymerisation using $O(10^4)$ zones in a stirred autoclave. The dynamic responses of sets of thermocouples arranged within the reacting fluid form a convenient basis for validation of the model. The complexities of compositional and temperature changes, together with the consequent reaction rates, are conveniently predicted from integration of sets of ordinary differential equations. The model parameters can be easily deduced from simple tracer visualisation tests.

Keywords: fluid mixing, network-of-zones model, runaway reaction, stirred vessel

INTRODUCTION

Many chemical reactions should be engineered to be carried out in stirred vessels, whose performance is crucial for successful manufacture. The basic concept of perfect mixing behaviour in an agitated reactor is often unacceptable especially for relating fast phenomena and their consequences. This is especially the case of exothermal run-away reactions, for which control cannot always be guaranteed by heat exchange alone. The safe operation of a stirred vessel in which an exothermal reaction is taking place is crucial for abating possible hazards. It is essential not only for the safety of the reactor itself but also perhaps for the neighbouring chemical plant as well. One example of a run-away reaction is the polymerisation of styrene taking place in a pressurised stirred vessel autoclave. The reaction is highly exothermal and above 120 °C can turn into a run-away one. The vessel jacket heat transfer is not then enough to provide reaction control and inhibitor is required to be quickly and suitably injected for reaction quenching. Stirred batch vessel mixing accompanied by run-away reaction has been analysed by 3-D networks-of-zones. A Pfudler impeller performance has been simulated by modification of an inclined blade impeller version of the networks-of-zones (Rahimi, *et al*, (1)). The simulations can provide detailed predictions of the spatial and temporal concentration fields of the reagents and products and a detailed picture of the simultaneous temperature field inside the vessel. Simulations are presented for a [2 x (10 x 10) x 60] configuration of networks-of-zones for an industrial pilot-plant polymerisation reactor.

The analysis to be presented here goes significantly beyond an earlier assessment of this reaction safety problem, which also used the same cell/zone approach (Kammel, *et al*, (2)). It also goes beyond our recent analysis of macro-segregation effects accompanying isothermal semi-batch operation (Rahimi and Mann, (3)). In this work, we show how to incorporate the following new complexities into the network-of-zones model:

- i. the injected quench fluid has a significant volume relative to the vessel fluid contents, so that the network zonal volumes must be adjusted for this.
- ii. the injectant will usually be at a different temperature, so that this effect must be included in the zonal heat balance
- iii. reaction quenching invariably has multiple chemical reactions (in this case 3) so that the several species balances will interact with the thermal field evolving from mixing of two miscible fluids at different temperatures, noting also that local zonal reaction rates will usually be strongly coupled with the evolving temperature field in 3D.
- iv. the zones at the wall will be continuously exchanging heat with the vessel jacket, further complicating the set of zonal heat balance equations.

FEATURES OF A TYPICAL LABORATORY RUNAWAY TEST

Results from a pilot plant experimental run using a Pfaudler impeller at 103 rpm are depicted in Figure 1. Times before quench injection are shown negative. As the insert diagram indicates, there are four thermocouples immersed in the liquid in the reactor. The two other thermocouples showing two different low temperatures are in the space above the liquid level. However, the four immersed thermocouples show very similar temperatures, indicating that the vessel contents are close to thermally homogeneous. The small differences that can be seen may reflect the small heat transfer effects at the wall.

During the time period to zero in Figure 1, the temperature is accelerating as the reaction begins to run-away. At 120 °C a quench is initiated, such that 10 dm³ of inhibitor are injected over a period of 4.6 s. Note that at the point of quenching, the two lower thermocouples have become engulfed by the expansion of the liquid in the vessel, as their temperatures suddenly increase. In the few seconds following the quench injection, the temperatures fall. The four upper thermocouples eventually exhibit a slow decline, indicating that the reaction has been totally stopped and the autoclave contents are now being cooled back down to the jacket temperature of 90 °C. Note also that the topmost thermocouple cools down in the ullage space, but the adjacent thermocouple shows intermediate behavior, possibly due to being immediately adjacent to the upper fluid interface following the increase in volume accompanying the finite volume quench injection.

THEORY

Networks-of-zones Assembly

The original networks-of-zones model (NoZ) based on the flow pattern generated by a mid-point radial turbine impeller divided the liquid phase into $2 \times N_i$ half-networks each consisting of $n \times n$ back-mixed zones. In this case the volume of the zones is assumed to be equal for each half-network. This approach can be simply adapted to map any flow patterns

generated by any mechanical agitator and this has been shown for an inclined blade impeller by the match between experimental visualisation results and theoretical (NoZ) predictions (Rahimi, *et al*, (1)). For the inclined blade impeller, the volume of each zone now depends on the spatial location of the zone and the inclined angle of the blades. The discharged flow from an up-pumping inclined blade impeller could be described as a flow from the impeller towards the liquid surface. The basic 3D topology of the networks-of-zones thus remains the same but the half-networks in the radial-axial planes are either compressed or stretched (Figure 2). An NoZ model for an axial plane with 2 x (10 x 10) zones has been adapted to capture the Pfaunder flow pattern as shown in Figure 2. The impeller is placed very close to the base (at $c=H/11.6$) and the conformal zone mapping is for an upper volume fraction of 0.88 (so lower volume fraction 1-0.88) with the flow from the impeller being directed upwards at an angle of 35° . The zone volumes are obviously related to the observed areas and for m tangential zones, the volume of each i,j,k zone is obtained by 3D geometry. The configuration in Figure 2 therefore comprises a total of $2 \times (10 \times 10) \times 60 = 12000$ zones. The discharge flow from the agitator, which is defined by an overall circulation convective capacity of the impeller given by $Q_L = KND^3$, is then equally distributed among the sets of nested liquid flow loops in each half-network as $q_L = KND^3/n.m$ (as there are n nested loops and m segments in the tangential k direction for a half-network).

Liquid Phase Balance Equations on the i,j,k Zone

The flow exchange for a general i,j,k zone is schematically shown in Figure 3. The main axial-radial liquid loop flow is accompanied by a tangential swirl flow described by two swirl flow coefficients β_L and β_R (clockwise and anti-clockwise) as well as in this particular case with isotropic turbulent exchange between all adjacent (nested) loops. Thus the flow input-output balance equations over the general i,j,k zone become:

$$V_{i,j,k} \frac{dX_{i,j,k}}{dt} = q_L \left(X_{i-1,j,k} - X_{i,j,k} + \mathbf{b} (X_{i,j+1,k} + X_{i,j-1,k} - 2X_{i,j,k}) + \mathbf{b}_L (X_{i,j,k-1} - X_{i,j,k}) + \mathbf{b}_R (X_{i,j,k+1} - X_{i,j,k}) \pm \text{reaction} \right) \quad (1)$$

where X is some monitored parameter. There would then be $2 \times (n \times n) \times m$ ordinary differential equations to be integrated for each monitored parameter. This basic balance equation covers most situations. However, when an injection of finite volume is present, the volume of the zones above the impeller becomes dependant on the volume injected (since the volumes of the zones beneath the impeller are fixed by the lower network as defined by the impeller clearance). This introduces an additional complexity handled by one more balance equation for the liquid zone volumes. In order to avoid differential complexity, the volume of the injected liquid is restricted to small increment for each integration step, so as not to disturb the integration solution. An additional term should be introduced into the balance equations to consider the volume change $\Delta V (X_{i,j+1,k} - X_{i,j,k})$, where $\Delta V = \frac{V_{inj}}{n^2}$ since only the upper half-network will be affected by this zone volume timewise adjustment. After each integration time step, the volume of the zones is corrected against the volume of the injection.

Zonal Balances on the Chemical Components

Reagents in this case are the reactant monomer A , the initiator I and a quenching agent Q . The liquid convectively and turbulently mixes all of them dynamically. At the same time, reaction is continuously taking place throughout all the zones. The reactant A reacts to the

polymer product by two steps (initiation and propagation) from which the first one is rate determining as the second step is very fast. The rate of initiation is a sum of chemical (*I*) and thermal initiation (*T*). The rate of chemical reaction of *A* is dependant on two terms and in this example depends on the initiator concentration:

$$r_{ci} = k_{1,0} e^{-\frac{E_1}{RT}} \left(\frac{C_I}{2} \right)^{0.5} + k_{2,0} e^{-\frac{E_2}{RT}} \left(\frac{C_I}{2} \right)^{0.5} \quad (2)$$

The thermal initiation only occurs for a temperature above 90-95 °C, it depends primarily on the reactant concentration C_A and the rate could be written as:

$$r_{ti} = k_{3,0} e^{-\frac{E_3}{RT}} C_A^2 \quad (3)$$

The overall rate of initiation is the sum of the chemical and the thermal initiation rates. At a temperature point of 120 °C the reaction tends to a run-away and the quencher has to be injected to prevent it. The quencher has two chemical tasks, to cancel the chemical initiation and to terminate the initiator. Once the quencher has chemically acted in this way, it then modifies the mechanism of the further reaction. The thermally induced kinetic expression no longer holds in the presence of quencher. Therefore a separate equation describes the subsequent rates of reaction:

$$r = k_{quench} C_A C_Q^{-1/4} \quad (4)$$

For the networks-of-zones model it has been assumed that once the quencher concentration in a given zone exceeds the concentration of the initiator, then the kinetics will switch to the quencher rate equation only. At this point, the initiator concentration will effectively drop to zero and the thermal initiation equation will no longer be valid (and therefore cancelled out from then onwards).

Zonal Temperature Balances

The temperature is a crucially important parameter in this particular reaction hazard simulation case. The circulating liquid in the vessel transfers heat convectively. Diffusion heat flow due to temperature difference is negligible because of the generally vastly turbulent flow in the reactor. Since the polymerisation reaction is highly exothermic, the heat locally generated by the reaction DH is used in all the zone temperature balances. Heat is transferred through the vessel wall firstly to reach the temperature necessary for thermal initiation (90°C) and secondly for cooling the vessel once above this temperature. This heat transfer would take place only at the boundary vessel wall and the base and for these zones, the following additional term is included in their heat balance equations:

$$Q = UA' \Delta T = UA' (T_{zone} - T_{jacket}) \quad (5)$$

where U is the local overall heat transfer coefficient, A' is the local zone heat transfer area and ΔT is the local temperature difference. The liquid flow rate in the jacket is assumed to be very high in order for temperature of the jacket to remain approximately constant. Liquid

surface heat transfer is insignificant because the pressurised reactor is closed throughout the batch.

PREDICTING NON-ISOTHERMAL MIXING BEHAVIOR

The use of networks-of-zones provides a simpler computation of this complex reaction hazard suppression because the simulation of the quenching behaviour relies only upon the integration of sets of ordinary differential equations (ODEs). There are 3 component balance equations for the chemical substances, which may be strongly coupled by non-linear reaction kinetics. There is an additional equation for zone temperatures and this variable T will often be strongly coupled via the Arrhenius temperature dependency of the chemical reaction kinetics. Thus for an $[2 \times (n \times n) \times m]$ network with c chemical components the solution requires $[2 \times (10 \times 10) \times 60] \times (3+1)$ equations to be integrated from the stated initial conditions. This model is much simpler than seeking the solution of the partial differential equations of the time-averaged Navier-Stokes equations (Brucato, *et al*, (4)). Apart from specifying a reasonable network size, the model parameters are the impeller convective circulation constant K , the turbulent exchange coefficient \mathbf{b} and the net swirl in the direction of rotation given by $\mathbf{b}_L-\mathbf{b}_R$ (implying isotropic turbulence if $\mathbf{b}_R=\mathbf{b}$). It is convenient to utilise the model to predict the zone temperatures for experimental results obtained from restricted sets of thermocouples placed strategically around the interior of a test vessel (whether laboratory or semi-tech scale). If the model can satisfactorily replicate such laboratory temperature response tests, then it can become a powerful tool for determining the quench injection requirements for a plant-scale vessel that can be reasonably guaranteed to ensure immediate and adequate suppression of runaway reactions. This approach will now be illustrated for some real results for a styrene polymerisation (although some key details are withheld for commercial reasons).

NoZ MODEL PARAMETERS FOR PFAUDLER AGITATOR

The flow components for each zone described earlier are now depicted in Figure 3, for the case when the axial-radial loop flow is outward (in the i direction). The model has been described in more detail elsewhere (Rahimi, *et al*, (1)). In flowing around an axial loop, the loop flows q_L are nested around upper and lower flow foci (located at (5,5) and (5,15) ie in the mid point of each square network assembly). Each loop in circulating flows outwards, upwards, inwards and downwards back towards the impeller. As well as experiencing this nested loop flow, each zone experiences a net through swirl flow (in the tangential direction) $\mathbf{b}_L-\mathbf{b}_R$, equivalent to $\mathbf{b}=\mathbf{b}_R$ if the turbulence is taken to be locally isotropic. It is a simple matter to define the NoZ parameters by visualisation of the mixing of an inert tracer (following the procedures outlined in detail earlier (Holden and Mann (5), Rahimi, *et al*, (1))). In such a tracer test case, there are no reactions, the tracer has a suitable colour to provide the visualisation and of course the mixing is isothermal. There is thus only a single component ($c=1$). Figure 4 then depicts a typical visualisation of a tracer mixing test in a glass vessel for a nigrosine dye (blue) using NoZ parameters as indicated in Table 1. For these values, one overall axial-radial internal circulation takes about 5.7 s and one complete swirl would require 7.3 s. The strong effect of the relatively slow swirl flow is immediately evident in the underneath plan views in Figure 4 (as would be seen experimentally using a 45⁰ mirror beneath the base of the vessel in any visualisation test (Rahimi, *et al*, (1))).

SIMULATING INCIPIENT RUNAWAY AND QUENCH INJECTION

The network-of-zones model can be applied throughout a reaction batch. With the reagents initially premixed, using the reaction kinetics for styrene polymerisation (Middle (6)), the model behaves like a perfectly mixed batch with the exception of the (few) wall zones which undergo heat transfer to the jacket. Figure 5(a) shows the predicted behaviour which applies for all the submersed thermocouples. This figure shows how the temperatures slowly accelerates as the batch reaction proceeds. At every instant, the heat produced by reaction is larger than the rate of removal at the autoclave walls, causing the temperature to constantly increase. The Arrhenius temperature dependency results in an acceleration of the timewise temperature gradient, more then offsetting the falling concentrations of reagents. At about 840 s, the fluid temperature has reached 120 °C, which is the normal trigger point for quench injection to stop the impending run-away.

Figure 5(b) then shows the predicted results of the quench injection as would be indicated by the four thermocouples which are immersed in the fluid. The concentration and temperature fields which evolve in 3D over a few seconds are obviously complex. This complexity is evidenced in Figure 5(b). In terms of thermocouple response, there is an injection over 4.6 s of “cold” quench material at 14.5 °C into the hot fluid (just rising beyond 120 °C). This cold fluid mixes turbulently and convects amongst the hot fluid and “shuts-off” heat-generation by reaction as the quench component is spread (also by fluid mixing) throughout the fluid in the autoclave.

The individual responses in Figure 5(b) make sense in a qualitative way in terms of the known fluid flow behaviour in the network-of-zones representing the stirred fluid. The injection zone is placed just in the upper sets of zones and the quench will mix upwards and swirl strongly (since $\beta_L - \beta = 0.9$). The detecting thermocouples are at a tangential angle of 120° and the fastest cooling is seen by the two central thermocouples. The greatest cooling is seen by TC5, which is next to the lowest thermocouple. The temperature dips to a 104 °C minimum at just after 6 s, reflecting the passage of the slug of “cold” quenchant. The thermocouple above it (TC4) shows less reduction and is slightly slower to fall and thus exhibits a later minimum at 7 s. The topmost thermocouple (TC3) experiences a lesser cooling, being further away from the centroid of the circulating and dispersing “slug” of quenchant. In remarkable contrast, the lowest thermocouple (TC6) of the four, sees so little of the quenchant over the first 3 s that it’s temperature actually increases by some 2°C before it begins to cool and be quenched. Thus it is evident that fluid mixing is such that the lower part of the vessel (i.e. those zones below the split between upper and lower portions of the flow pattern) quench more slowly and their runaway condition persists until the quenchant is mixed below the upward/downward flow separation line. The lowest thermocouple (TC6) shows then the highest minimum (just below 112°C) at approximately 7.5 s after the injection.

After these minima, reflecting the swirling passage of the quenchant, the thermocouple responses show some oscillations in converging finally to the fully mixed temperature condition. This is closely approached after some 20 s from initial injection. This represents about 4 internal turnovers based on an impeller circulation constant value of $K=0.47$ (Metzner and Norwood, (7)).

BEHAVIOUR BEYOND THE QUENCH INJECTION

In terms of a complete quench, this has not been achieved since the overall temperature drop of 5.5 °C from the original 120°C is sufficient for polymerisation reaction to continue at a finite rate, since in Figure 5(b) beyond 20 s, temperature is continuing to climb, albeit very much more slowly than at the trigger temperature of 120°C. This also reflects the fact that the quench completely suppresses the autocatalytic polymerisation reaction that has built up in the earlier part of the batch. The average reaction rate of polymerisation during the fast changing quench mixing is shown in Figure 6. It can be seen that the overall reaction rate falls rapidly from its initial value of 2.52 at the quench trigger to a very low value of $1.44 \cdot 10^{-5}$ within the initial quench mixing period. This indicates that much more than 99% of all zones are fully reaction quenched within this period.

ONSET OF THE SECOND RUNAWAY

After 25 s, as Figure 5(b) has shown, the autoclave is both compositionally and thermally almost perfectly mixed. However, the still finite polymerisation rate indicated in Figure 6 means that the reaction can still continue to build-up and eventually there will be a second runaway. The simulated behaviour following the quench injection is then depicted in Figure 7, where it is directly compared with an experimental result. The second runaway is predicted to occur about 130 min later. Without a further quench, the complete runaway leads to a final very high temperature of 600 °K. The model thus provides for useful predictions before, during and after the quench. Interestingly, the time location of the second runaway depends crucially upon the quench behaviour. It is evident, both experimentally and theoretically that changes in dynamic mixing over a few seconds can cause the runaway times to vary by many tens of minutes. It is of course important not to neglect the subsequent runaway, otherwise a reactor accident may take place following an apparently successful and safe initial quench.

CONCLUSIONS

- The complexities of fluid mixing with multiple chemical reactions and simultaneous quenching by a miscible cold slug of a chemical “stopper” have been successfully simulated by a network-of-zones model with $O(10^4)$ zones.
- Concentration and temperature profiles in 3D are integrated by simple sets of ordinary differential equations. Consequently reaction rates in 3D are also predictable if the detailed chemical reaction kinetics are known. An example for styrene polymerisation using a Pfaudler impeller has been used for successful illustration.
- In monitoring real examples of runaway reaction, quenching data can be conveniently acquired from sets of thermocouples in the reactor. The dynamic responses of these thermocouples form a basis for validation of the theory.
- Parameters for the network-of-zones model can be obtained by simple tracer visualisation tests.
- Following a successful initial quench simulation, the model can be used to predict any subsequent runaway events

NOMENCLATURE

<p>A' heat transfer area, m²</p> <p>c impeller clearance, m</p> <p>C_A concentration of reactant A, mol m⁻³</p> <p>C_I concentration of initiator I, mol m⁻³</p> <p>C_Q concentration of quencher Q, mol m⁻³</p> <p>D impeller diameter, m</p> <p>E_1 activation energy</p> <p>E_2 activation energy</p> <p>E_3 activation energy</p> <p>H liquid level in the vessel, m</p> <p>i radial zone position</p> <p>j axial zone position</p> <p>K overall impeller flow constant</p> <p>k tangential zone position</p> <p>$k_{1,0}$ reaction rate constant</p> <p>$k_{2,0}$ reaction rate constant</p> <p>$k_{3,0}$ reaction rate constant</p> <p>k_{quench} reaction rate constant in presence of inhibitor</p> <p>m number of zones along the vessel perimeter</p> <p>N impeller speed, rps</p> <p>N_i number of impellers</p> <p>n number of zones in axial/radial plane (half network)</p> <p>Q heat transfer</p> <p>Q_L overall liquid circulation by the impeller, m³ s⁻¹</p> <p>q_L liquid flow rate in nested (axial/radial) flow loops, m³ s⁻¹</p> <p>R universal gas constant</p> <p>r reaction rate in presence of inhibitor</p> <p>r_{ci} chemical reaction rate</p> <p>r_{ti} thermal reaction rate</p> <p>T vessel diameter, m</p>	<p>T temperature, °K</p> <p>T_{jacket} temperature of the vessel jacket, °K</p> <p>$T_{i,j,k}$ zone temperature, °K</p> <p>ΔT temperature difference</p> <p>t time, s</p> <p>U overall heat transfer coefficient, W/(m²°K)</p> <p>$V_{i,j,k}$ zone volume, m³</p> <p>V_{inj} zone volume, m³</p> <p>ΔV zone volume change, m³</p> <p>X monitored parameter</p> <p>Greek letters</p> <p>b lateral turbulent exchange coefficient</p> <p>b_I turbulent exchange coefficient in the impeller plane</p> <p>b_L clock-wise swirl coefficient</p> <p>b_R anti-clock-wise swirl coefficient</p> <p>Indexes</p> <p>A reagent A</p> <p>ci chemical initiation</p> <p>I reagent I (initiator)</p> <p>Q reagent Q (inhibitor)</p> <p>ti thermal initiation</p>
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Table 1: Networks-of-Zones flow parameters

<i>Networks-of-Zones flow parameters</i>		
<i>Parameter</i>	<i>notation</i>	<i>Value</i>
Impeller circulation constant	K	0.47
Turbulent exchange coefficient	β	0.1
Clock-wise exchange coefficient	β_L	1.0
Anti-clock-wise exchange coefficient	β_R	0.1
Axial turbulence near the impeller	β_I	1,0

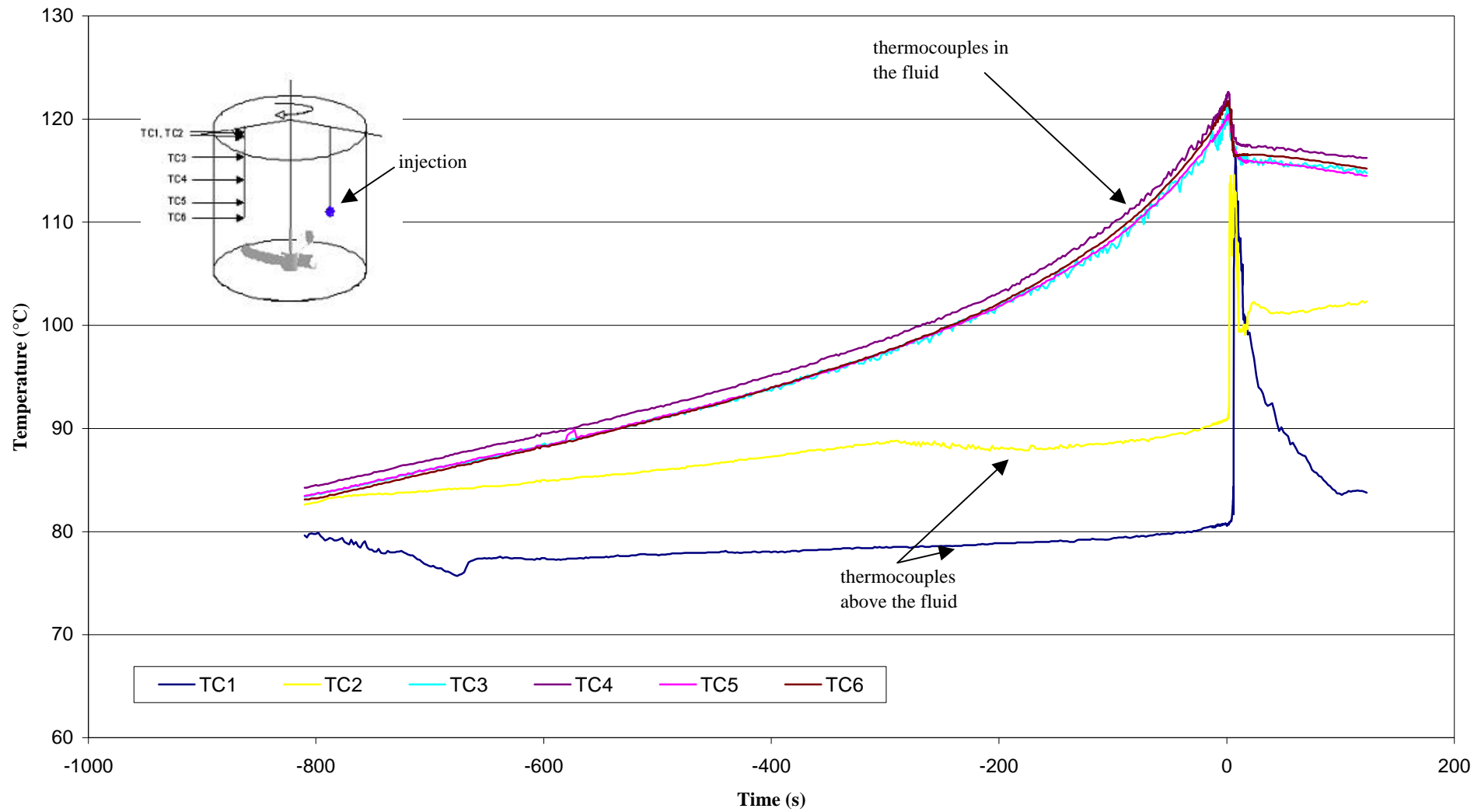


Figure 1: Experimental laboratory quench result – temperature profile (impeller speed 103 rpm)

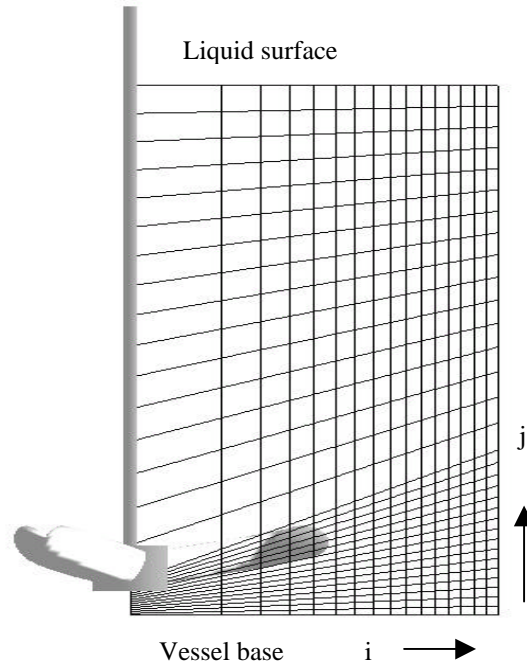


Figure 2: 2D Axial/radial NoZ configuration for Pfaudler agitator

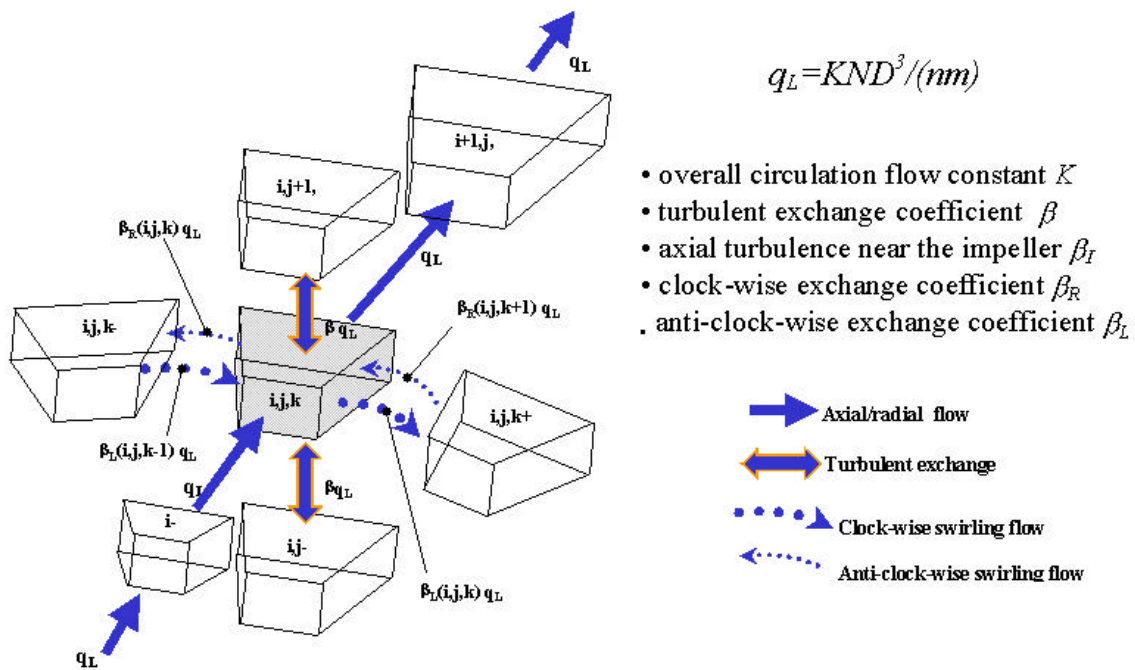


Figure 3: The general i,j,k zone flow exchanges

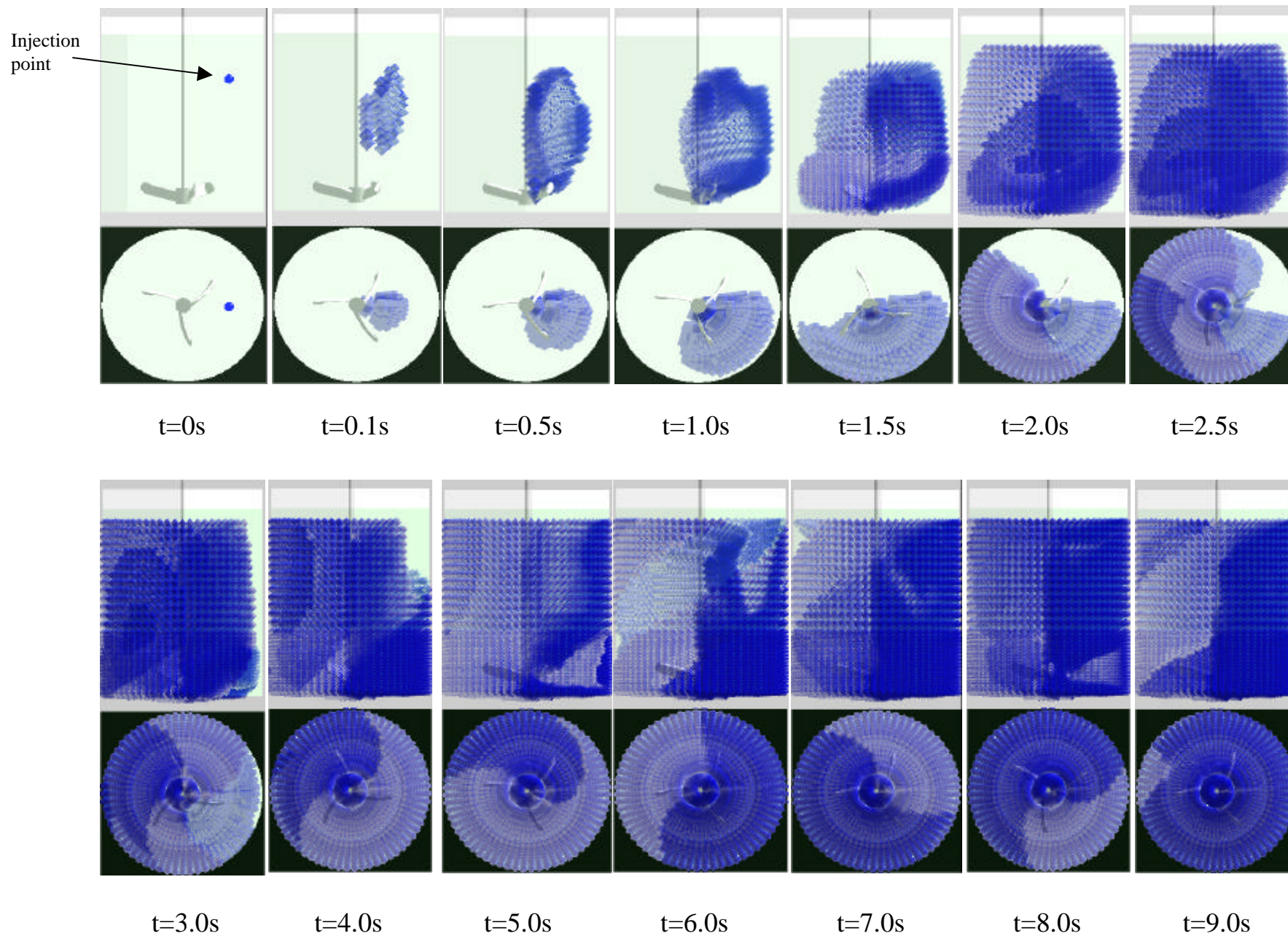


Figure 4: Networks-of-zones simulation of passive tracer pulse using Pfaudler agitator

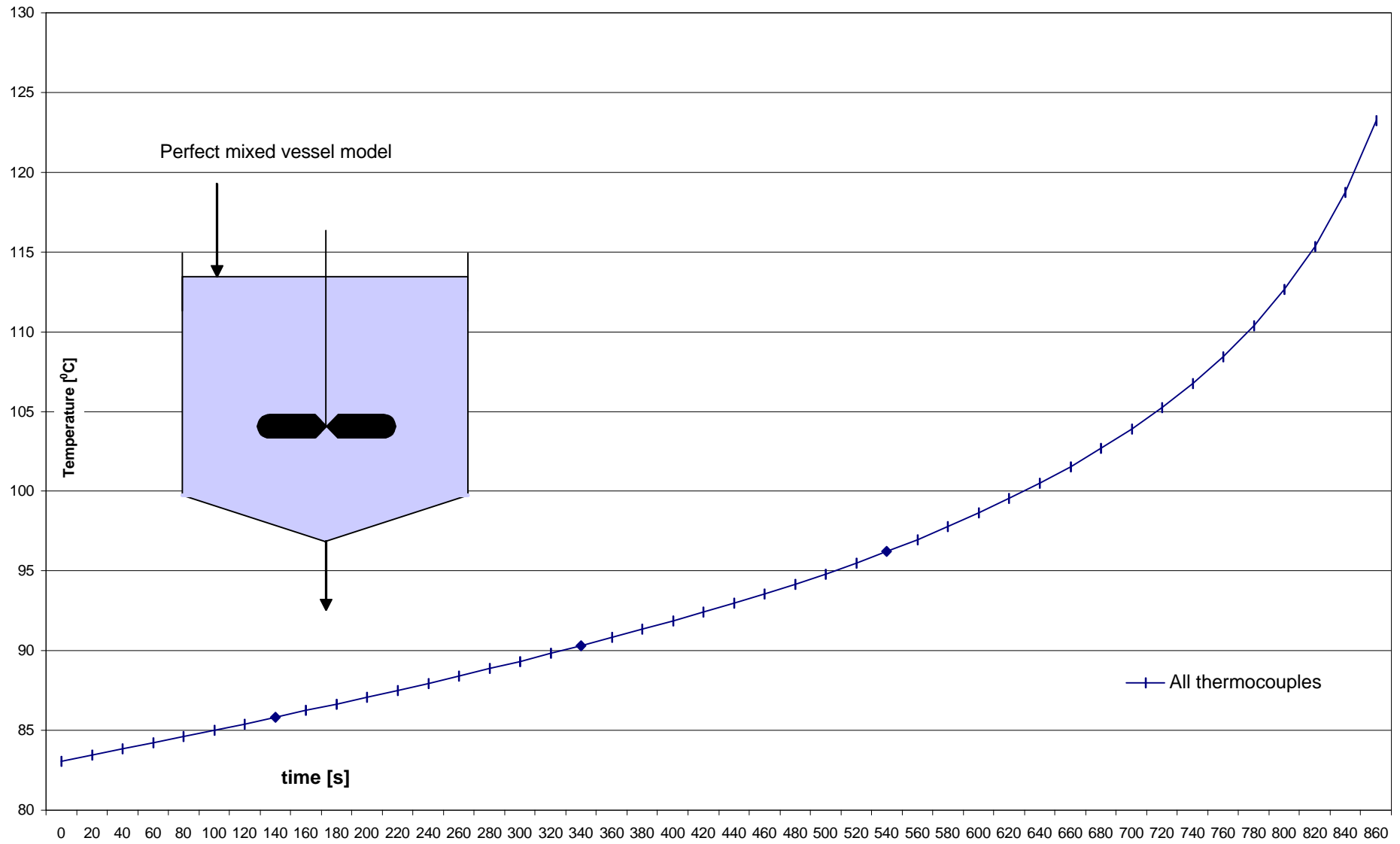


Figure 5a: Temperature mixing curve. Perfect mixing model

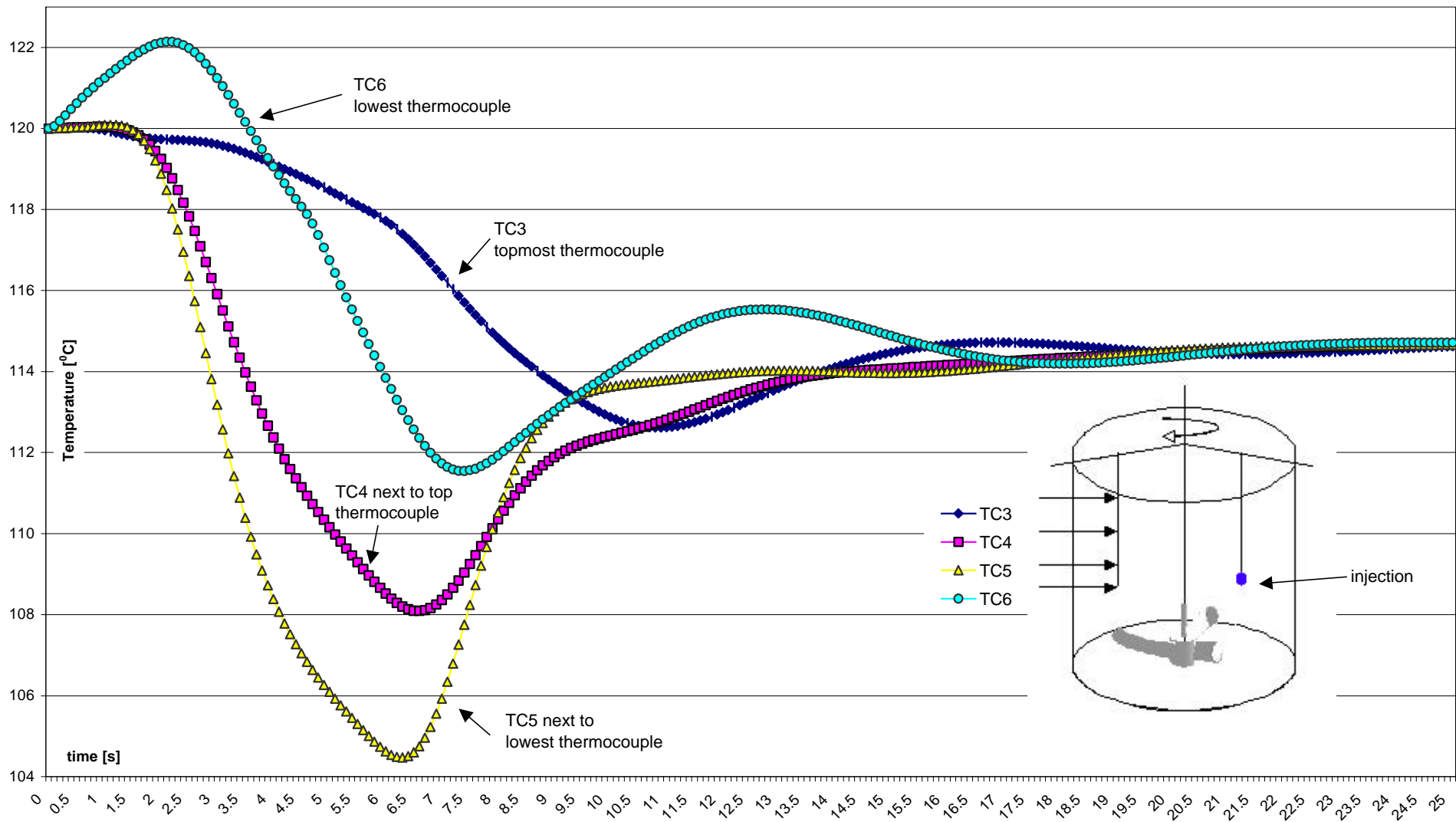


Figure 5 b: Predicted temperature mixing curves by NoZ (injection of inhibitor at trigger point), stirrer speed 103 rpm

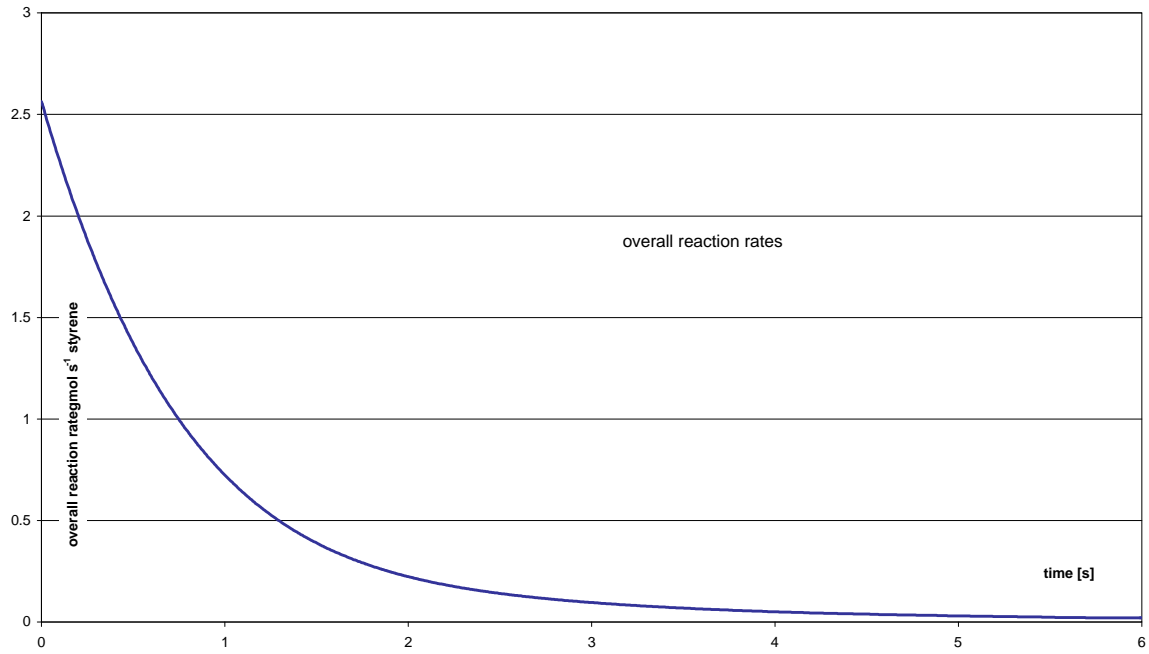


Figure 6: Overall reaction rate after the quenching agent has been injected

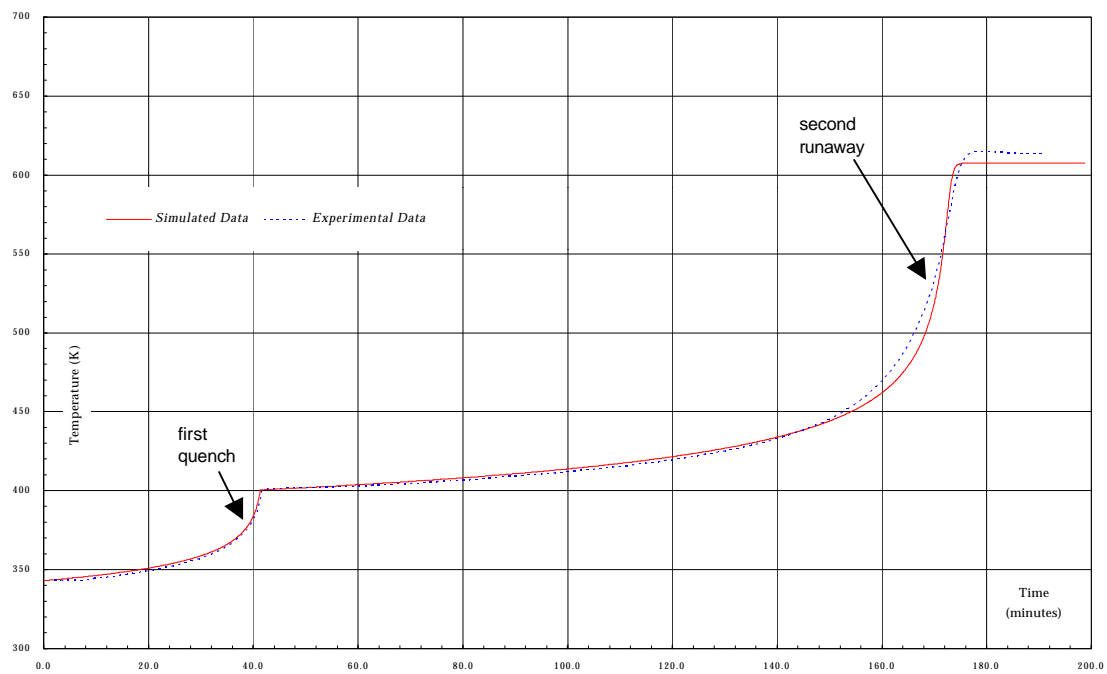


Figure 7: Autoclave temperature profiles