

Experimental Investigation and High Resolution Simulator of In-Situ Combustion Processes

Quarterly Report

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Abstract

Accurate simulation of in-situ combustion processes is computationally very challenging because the spatial and temporal scales over which the combustion process takes place are very small. In this current and **fourteenth** report, we report on our continued numerical experimentation with the Virtual Kinetic Cell and our continuing experimental program.

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1. Introduction

In-situ combustion, or air injection, is the process of injecting oxygen into oil reservoirs to oxidize the heaviest components of the crude oil and enhance oil recovery through the heat and pressure produced. The emphasis of this work is to study and model numerically in situ combustion processes. The ultimate objectives are to provide a working accurate, parallel in situ combustion numerical simulator and to better understand the in-situ combustion process when using metallic additives and/or solvents combined with in situ combustion. For this purpose, experimental, analytical and numerical studies are conducted.

This report presents results of the second quarter of the fourth year of this project.

2. Executive Summary

2.1. Personnel

Current personnel include Prof. Margot Gerritsen (PI), Prof. Tony Kavscek (Co-PI), Dr. Louis Castanier (Technical manager), as well as our graduate student Mr. Rotimi Awoleke (MSc student). We have also continued collaboration with Mr. Morten Kristensen (PhD student) from the Technical University of Denmark, and his advisors Prof. Erling Stenby and Prof. Michael Michelsen.

2.2. Important accomplishments

Numerical work: development of the Virtual Kinetic Cell Model

In previous reports we outlined the design of a Virtual Kinetic Cell model (VKC), which we are using to design suitable numerical integrators for the stiff kinetics in ISC processes, and to investigate the interaction between kinetics and phase behavior. The Virtual Kinetic Cell (VKC) was developed in [1] and further extended in [2]. We implemented two types of reaction models: a minimal model, which includes the minimal realistic set of 6 components and corresponding reactions to represent ISC behavior as given below, and a SARA-based model containing 14 components. Both models were discussed in detail in previous quarterly reports. The SARA model is also detailed in [3-5].

Last quarter we specifically discussed the extension of the VKC model to include full phase behavior through cubic equations of state (such as Peng-Robinson), and showed preliminary comparisons between constant K-values and Peng-Robinson for various numerical experiments. In this report we further discuss the sensitivity of kinetics to phase behavior as this could potentially have large implications on the modeling of ISC processes in realistic settings.

Ignition/extinction behavior

In order to investigate the ignition/extinction behavior further we carry out a sequence of experiments to map out the parameter space in terms of ignition and extinction regimes. As key parameters we choose the air flow rate and the heat loss rate. If non-dimensionalized the kinetic cell equations will depend on a set of non-dimensional groups with Damköhler numbers measuring the relative importance of reactions to convection and a heat loss number. Varying the air flow rate and the heat loss rate effectively results in varying an overall Damköhler number and the heat loss number.

To study ignition/extinction behavior we must first define what we mean by ignition. Since the kinetic cell is a batch-type experiment with a continuous feed of air, the steady state always corresponds to all the oil being consumed and only the injection gas left in the cell. The paths taken to reach the steady state can be very different. In the simulations discussed below we heat up the cell to a specified temperature, T_{spec} , and then keep a constant cooling temperature at this level. If sufficient heat is evolved from reactions to increase the cell temperature to a threshold temperature, $T_{thres} > T_{spec}$, we then characterize that as an ignited state. The areas of the parameter space (the parameters being injection rate and heat loss rate), where the maximum temperature during a simulation, T_{max} , is above T_{thres} , define the ignition regimes. The boundaries of the regimes correspond to $T_{max} = T_{thres}$, but we will refer to them as ignition/extinction curves.

3. Experimental

The experimental program is focused on the proof of concept for (i) water-soluble metallic salts to improve fuel lay down and enhancement of combustion performance as well as (ii) a new recovery concept that combines cyclic solvent injection and in-situ combustion to remove any solid precipitation resulting from the solvent.

One setting in which metallic additives are attractive is heterogeneous and fractured reservoirs. The catalytic effect engendered by additives may aid combustion in such difficult reservoirs. We are studying reservoir core with residual oil and an ample supply of crude oil. Scanning electron microscopy (SEM) confirms that the rock grains are consistent with sandstone lithology. The crude oil is a 19.7°API sample. This effort has been ongoing over the past 3 quarters.

Experiments have been conducted using crude oil and sand from a quarry, crude oil and reservoir matrix, and reservoir matrix alone. Both ramped temperature oxidation (i.e., kinetics cell) to obtain the kinetics of combustion and combustion-tube runs have been conducted. The former helps in providing information about the reactions occurring, their rates and their temperature and pressure dependencies. The latter helps in understanding whether a stable combustion front is formed as well as the spatial and temporal propagation of such a fully-developed combustion front.

Figure 1 is a graphical summary of the experimental equipment. The combustion tube measures the ability of a combustion front to propagate through a given combination of crude oil, water, and porous medium. The kinetics cell is used to characterize activation energies of combustion as well as oxygen consumption. The combustion tube, or alternately the kinetics cell, is coupled to a gas analyzer, traveling thermocouple, and data logging system.

Oxygen and nitrogen are provided by gas cylinders and metered using a mass flow controller. Temperatures are recorded in the kinetics cell tests as measured in the center of the cell. Air is injected from the bottom of the cell. Prior to injection, air flows through coiled 3.2 mm (1/8 in.) tubing and is preheated. On the top of the cell air exits and the temperature is measured. In combustion tube runs a thermal well is placed within the pack and a traveling thermocouple used to measure temperature along the length of the combustion tube. Air is injected from the top of the tube in a gravity-stable fashion. In both setups, a gas analyzer collects effluent gas composition and measures oxygen, carbon dioxide, carbon monoxide, and methane concentration. Measurements are recorded once per minute.

The oil sample was used as received. It is 19.7° API and asphaltenic. The reservoir matrix as received still contained hydrocarbon.

4. Results and discussion

4.1. Numerical work: development of the Virtual Kinetic Cell Model

In this section we carry out studies to explore the sensitivity of the kinetics to phase behavior and compare constant K-values vs an EoS approach based on the Peng-Robinson equation. We consider both the minimal reaction model and the SARA based reaction model.

We consider the minimal reaction model with $T_{\text{spec}} = 473\text{K}$ and $T_{\text{thres}} = 500\text{K}$. Figure 2 shows ignition/extinction regimes using the K-value and Peng-Robinson phase behavior models, respectively. Three separate cases are highlighted. At low air flow rates combustion is not sustained, whereas at high air flow rates the oil components are stripped from the oil phase before they react. Intermediate flow rates lead to ignition when the heat loss rate is low. Increasing the heat loss rate leads to extinction. Clearly, the two phase behavior models give different ignition regimes. At the lower branch of the ignition regime the two models predict similar behavior. When the air flow rate is increased, the increased volatility of the oil, as predicted by the K-value approach, leads to earlier extinction. We note that for the SARA reaction model the two phase behavior models predict similar behavior at the lower branch, but in this case the K-value model leads to an extended region of ignition for high flow rates compared to using the Peng-Robinson model. In this case, with the data available, the K-value approach predicts a less volatile saturates component compared to the Peng-Robinson approach, which results in an improved LTO of saturates in the K-value approach.

4.2. Experimental work

Four kinetic ramped-temperature-oxidation (i.e., kinetics cell) experiments have been performed to date. The first was carried out on a mixture of sand, kaolinite, crude oil and water. It is referred to here as a ‘mixture’. The air supply pressure was 50psig. The second experiment was on the crushed reservoir material at a supply pressure of 50psig, the third also on the crushed reservoir core at 200psig and the fourth, purely out of curiosity, on the remains from the reservoir material after any toluene-soluble material has been removed (henceforth referred to as ‘washed core’), also at 200psig supply pressure.

The data for oxygen consumed implies that low-temperature oxidation (LTO) occurs at about 350°C and high-temperature oxidation (HTO) at about 485°C. An analysis of the effluent gas data using the Arrhenius equation and numerical integration results in E_a/R (ratio of activation energy to gas constant) value of about 4500K for the LTO and about 6700K for the HTO as summarized in Table 1. These values are consistent with others in the literature for viscous oil and indicate that this system should be a good candidate for combustion.

This system appears to be sensitive to the supply pressure of air and this is a concern for field operations. At 50psig we did not bring about complete combustion. Because combustion is very much dependent on the partial pressure of oxygen, a low supply pressure results in a low oxygen partial pressure and hence the incomplete combustion. Increasing the air supply pressure to 200psig resulted in a complete combustion.

Table 1. Summary of kinetic parameters as measured using ramped temperature oxidation.

	Pressure (psig)	E_a/R (K) LTO	HTO
Mixture	50	6700	4500
Mixture+Additive	50	7600	56000
Crushed Core	200	8000	1800
Crushed Core+Oil	200	7400	7300
Crushed Core+Oil+Additive	200	6000	10000

We also conducted a significant number of tube runs to verify that a combustion front could be propagated through this particular matrix/crude oil system. The makeup of the porous medium and oil content mirrored, to some extent, that of the kinetics (RTO) tests. For simplicity of presentation, we group the tube runs according to the order in which they were performed. We have not tested the effect of metallic additives on combustion propagation performance because the core material already contains iron in the form of pyrite. As iron is a known catalytic agent for ISC, we avoided confusion of the natural catalytic effect of the matrix with that induced by adding iron.

- Tube run 1, the combustion tube was packed with crushed reservoir material only. Ignition was successful and the combustion front propagated. The air flux was 3 SLPM.
- Tube run 2, this experiment consisted of an artificial mix of quartz sand and kaolinite. Oil was added as well as water. By weight, the mixture consisted of 83.3% sand, 3.9% kaolinite, 7.8% oil, and 5% water. The air flux was again 3 SLPM. The tube ignited well and the combustion front propagated about 10% of the tube length, but then stalled. The post mortem analysis suggested excessive banking of mobilized oil that inhibited oxygen flow to the combustion front.
- Tube run 3 was made with the objective of investigating the effect of heterogeneities on combustion process efficiency. It was also designed to reduce oil banking and allow increased air flux in the system if such a need arises. The packing of the tube is unique: the first 10 cm of the core adjacent to the ignitor were packed with an oil/water/sand and kaolinite mixture similar to that used in run two, the next 16 centimeters down were packed with crushed reservoir material only, the next 60 centimeters were packed with pieces of reservoir core with crushed core/oil mixture packed around the pieces, the bottom of the tube was packed with coarse quartz sand to facilitate oil production. The combustion front did progress and we categorize the burn as successful.

We now present more detail about the third tube run. After ignition, the air flux was set to 3 SLPM. After 60 min, the air flux was increased to 6 SLPM for the duration of the experiment. The effluent gas production is presented in Figure 3. The variations seen on the gas composition plot are directly related to the air flux, namely when the air rate was low, the amount of oxygen consumed decreased as did the production of carbon oxides. The reverse behavior was experienced when the air flux was increased. Some of the flat portions in Figure 4 arise because gas flow to the gas analyzer was suspended periodically when pressure drop across the analyzer exceeded 3 psi. After relief of pressure, flow to the analyzer was resumed.

The temperature data are summarized on Figure 4. In short, the temperature front stopped as the air flow rate was at 3 SLPM or lower and the temperature front progressed when the air flow rate was above this level. The various heterogeneities in the matrix did not seem to show an effect on the front movement. Despite the scattered nature of the peak temperature on the Figure 4, the combustion front progressed rather smoothly given the heterogeneity and oxygen requirements of the system.

Another observation is that the amount of air consumed is quite large. The air used is estimated as follows for Tube Run 3. At say 45 cm from the ignition point, the volume swept is the surface of the tube (44 cm^2) multiplied by the distance traveled by the front (45 cm). Hence the volume is 1980 cm^3 . The amount of air injected to this point is $1.74 \times 10^6 \text{ cm}^3$. The average concentration of O_2 in the effluent gas is 4%, by mole. Hence, 16.7 % of O_2 is utilized. This equates to an air

requirement of 860 standard m³ to burn a m³ of rock. This is substantially more air than usually needed for similar gravity oils. For instance, some Canadian systems require 360 m³ of air per m³ of reservoir. This large air consumption likely results from the presence of residual hydrocarbon on the reservoir matrix provided for the tests. This extra hydrocarbon results in a greater amount of fuel that in turn consumes a large volume of oxygen for proper combustion.

5. Conclusions

We have made excellent progress with study of the sensitivities of kinetics to phase behavior representations. We have shown clearly that kinetics, and possibly performance prediction of ISC processes, can depend very strongly on phase behavior and extreme care must be taken when implementing a ISC model. We emphasize that in the current work we have emphasized robustness of the algorithm, but we plan to address efficiency in the near future. We have also started implementing the kinetics solver into our 1D In-Situ Combustion code.

Regarding the experimentation, future work will involve the following tasks:

- Completion of the post mortem analysis of tube run 3 described above
- The kinetics tests showed effects from the pressure of the air supplied. A high pressure (1000 psi) kinetics test is planned to obtain kinetics at high pressure and to check this behavior versus our expectation that the combustion reactions are first order in oxygen partial pressure.
- A paper on the cyclic solvent/combustion process will be completed and readied for publication as a means of technical transfer.

Papers published this quarter

Awoleke, R. "An Experimental Investigation of In-Situ Combustion in Heterogeneous Porous Media" SPE Western Region Paper Contest, Apr. 4, 2007. Long Beach CA

J. V.Lambers, M. G. Gerritsen , and B. T. Mallison, "Accurate Local Upscaling with Variable Compact Multi-Point Transmissibility Calculations", Computational Geosciences, 2007.

References

1. Morten R. Kristensen, Margot Gerritsen, Per G. Thomsen, Michael L. Michelsen and Erling H. Stenby, 2006, "Efficient Integration of Stiff Kinetics with Phase Change Detection for Reactive Reservoir Processes", Transport in Porous Media

2. Morten R. Kristensen, Margot G. Gerritsen, Per G. Thomsen, John B. Jorgensen and Erling H. Stenby, 2007, Coupling Chemical Kinetics and Flashes in Reactive, Thermal and Compositional Reservoir Simulation, SPE 106218: Presented at the SPE Reservoir Simulation Symposium, Houston, Texas, February 26-28

3. N. P. Freitag and B. Verkoczy, 2005, Low-Temperature Oxidation of Oils in Terms of SARA Fractions: Why Simple Reaction Models Don't Work, Journal of Canadian Petroleum Technology, 44, 2, 54-61

4. Norman P. Freitag and D. R. Exelby, 2006, A SARA-Based Model for Simulating the

Pyrolysis Reactions That Occur in High-Temperature EOR Processes, *Journal of Canadian Petroleum Technology*, 45, 3, 38-44

5. Y. Ren, N. P. Freitag and N. Mahinpey, 2005, A Simple Kinetic Model for Coke Combustion During an In Situ Combustion ISC Process, Presented at the 6th Canadian International Petroleum Conference, Calgary, Alberta, June 7-9

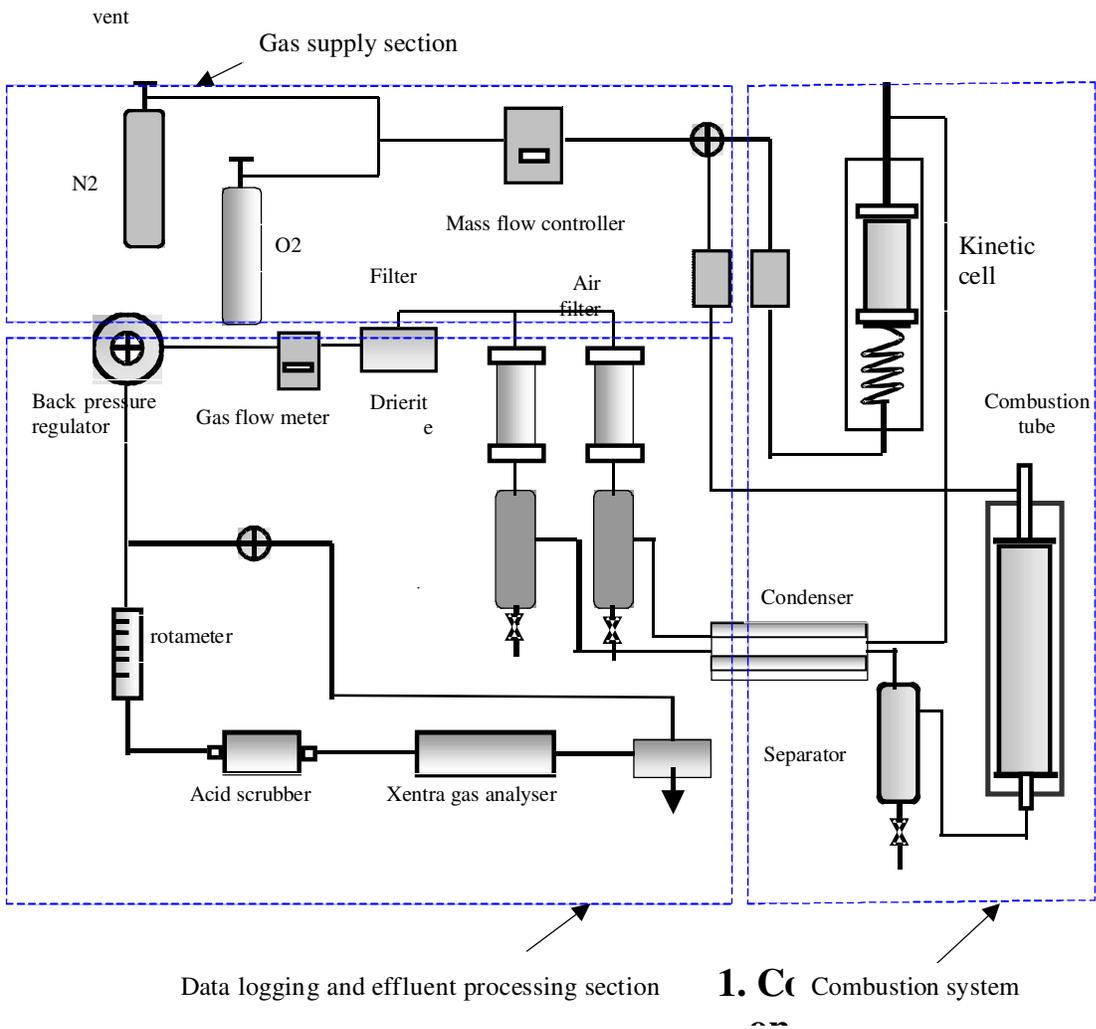


Figure 1. Experimental set-up for kinetic cell and combustion tube experiments.

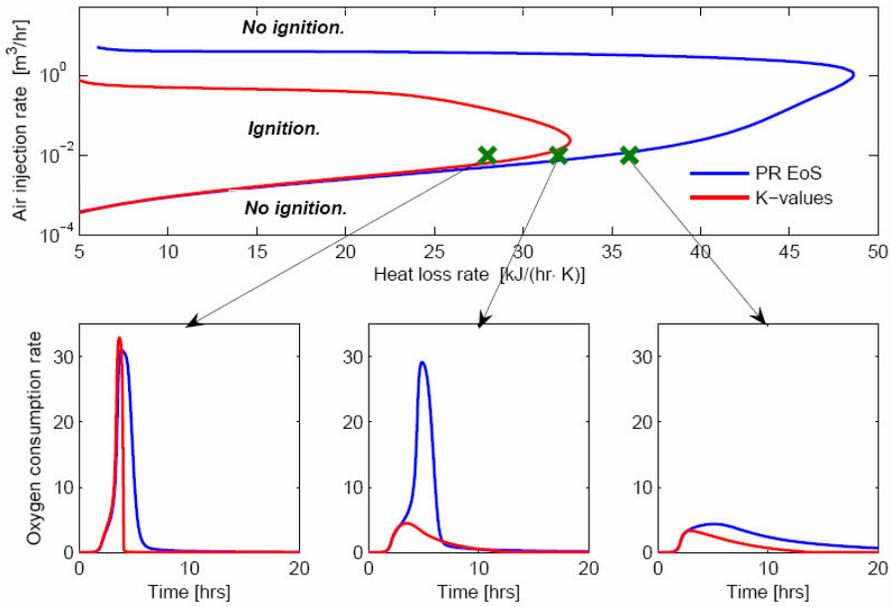


Figure 2. Ignition/extinction regimes as a function of air injection rate and heat loss rate for the minimal reaction model. Regimes are shown for K-value based and PR EoS based phase behavior.

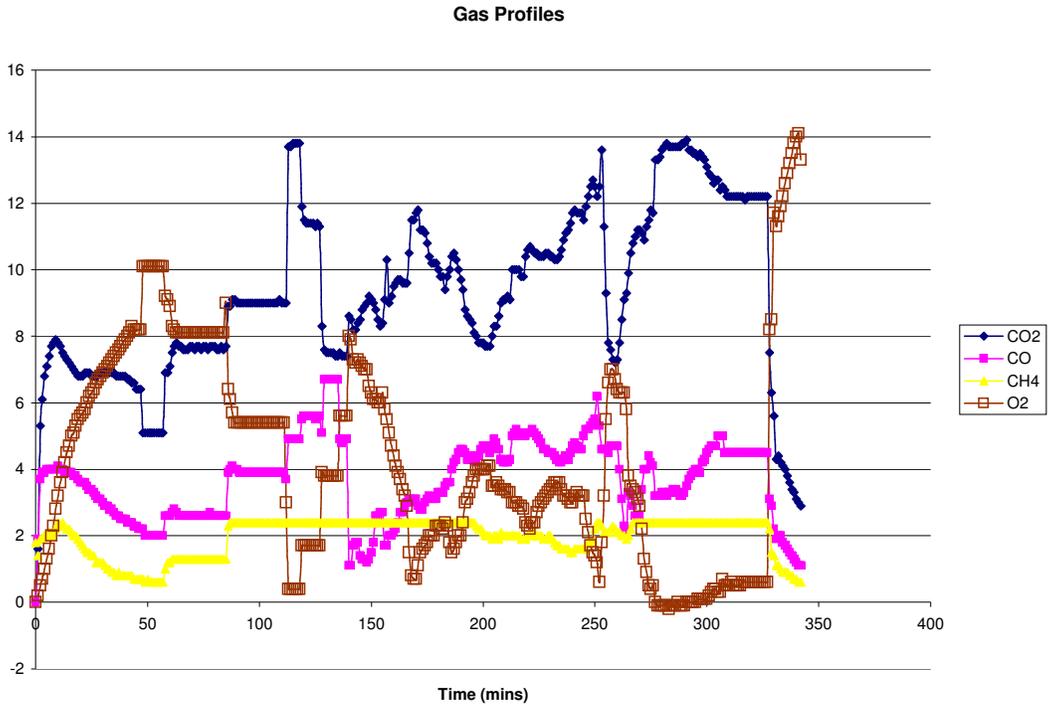


Figure 3. Effluent gas profiles from tube run 3: heterogeneous pack.

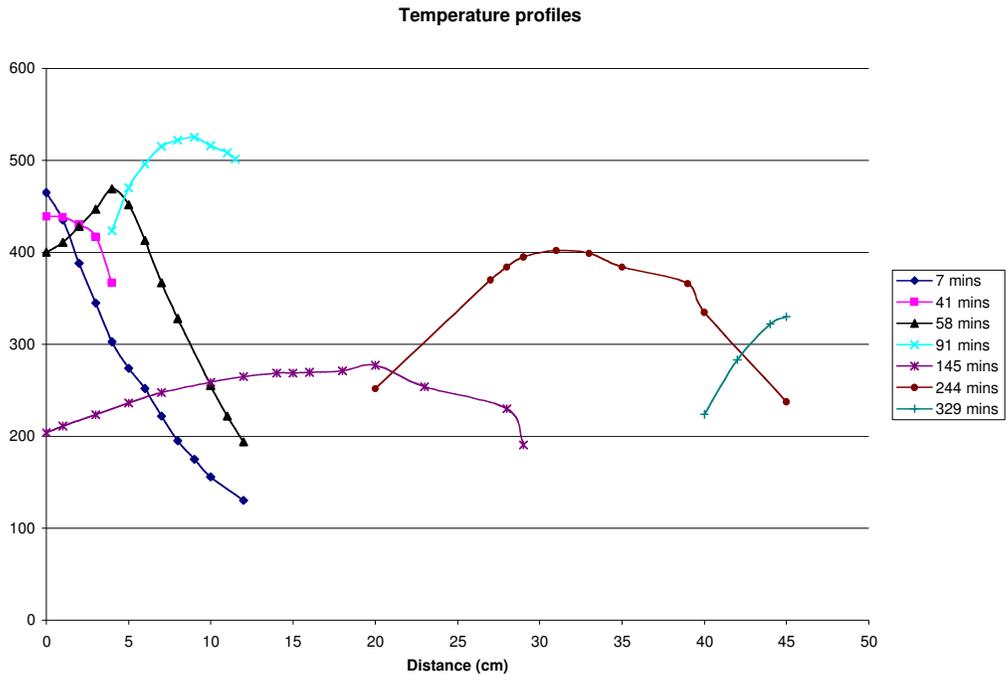


Figure 4. Axial temperature profiles from tube run 3, heterogeneous pack.