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Crude Oil Fouling: Fluid Dynamics, Reactions and Phase Change

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Abstract

In the present study, the fluid dynamics and phase behavior of crude-oil fouling in a closed-end heat-exchanger is studied. The deposition process associated with fouling is assumed to be due to two routes: asphaltene precipitation, and a two-step chemical reaction. The SAFT- γ Mie theory is employed to describe the phase behavior of an asphaltene-containing crude oil system, which comprises pseudo-components ($C_{13} \sim C_{20+}$). The predicted phase equilibrium constants are used to quantify the asphaltene precipitation rate. A computational fluid dynamics framework is then used to simulate the fouling process, accounting for the multiphase flow dynamics, heat transfer, and the two deposition routes. Fouling is simulated due to the two routes individually and in concert. In the latter case, it is found that the interaction of the two routes is due to the fouling layer adhering to the heat-exchanger walls, which influences heat transfer from the hot walls to the cooler oil in the bulk. The delicate interplay between heat transfer and fluid dynamics, which accompanies the flow, leads to enhancement and suppression of chemical reaction- and precipitation-driven fouling, respectively, and an overall rise in the fouling rate.

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Nomenclature

K	equilibrium constant
ΔH	precipitation enthalpy
T	temperature

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P	pressure
D	diameter
D_d	diffusion coefficient
R	the universal gas constant
J	the mass flux from the oil phase to fouling phase
ρ	density
η	dimensionless function
χ	the weight fraction of each component of the mixture
L	length
L_x	the number of moles present for each phase
θ	a parameter that depends on L_x
n	the normal vector to the tube walls
r	the reaction rate
k	reaction rate constant
C	species concentration
A'	the pre-exponential factor
E_{act}	the activation energy
m, n, l	the orders of the reactants and precursors, respectively

1. Introduction

In oil refineries, the relatively cold crude oil is heated up to high temperatures in preheat trains (PHT) of distillation units. Commonly, the heavy compounds in the crudes tend to phase-separate out via physical or chemical processes and deposit on the walls of heat-exchangers¹. This so-called crude oil “fouling” impairs drastically the thermodynamic and hydrodynamic efficiency of heat exchangers, which causes a major obstacle in the oil industry for many decades; no efficient solution to this problem has been identified yet.

It has been recognized that crude-oil fouling involves complex phase transfer usually driven by hydrocarbon oxidation/auto-oxidation and asphaltene precipitation². The asphaltene precipitation is induced by temperature, pressure and concentration fluctuations of the crudes. The hydrocarbon oxidation and auto-oxidation takes place when the temperature and crude-containing oxygen concentrations reach a certain level to overcome the activation energy. Previous studies^{3,4} observed that these two routes interact each other: the chemical reaction route was suppressed while the precipitation route was enhanced. A better understanding of this interaction could help to develop efficient fouling mitigation strategies.

Prior to developing such an understanding, the physical and chemical models need to be well-established. In the majority of asphaltene precipitation models, the asphaltene-crude oil system was treated as a solid-liquid thermodynamic equilibrium⁵. The phase equilibrium is expressed as the equality of chemical potential for each component in all phases and characterized by a phase equilibrium constant, which relates the solid fraction to liquid fraction of a component in the mixture. In order to predict this constant, the solid phase is often described by an activity-coefficient model based on an ideal or regular solution theory, whilst, the liquid phase is modelled using regular solution theory, Flory-Huggins theory, or via an equation of state (EOS)⁵.

Recently, the associating EOS, e.g. Statistical Associating Fluid Theory (SAFT), has been established and applied to describe the liquid-liquid equilibrium of asphaltene-containing fluids^{6,7}. The SAFT views molecules as chains composed of interacting spherical segments, monomers, with possible short-range association sites. The interactions between monomer segments are described via intermolecular potentials which are assumed to have three main contributions: dispersion and repulsion of individual segments, chain contributions from the bonds between the segments, and contributions due to association. The SAFT explicitly takes polarity into account, thereby reducing the need for the development of mixing rules and binary interaction parameters like classical EOSs.

Chemical reaction fouling is more complicated since the oxidation and auto-oxidation of heavy hydrocarbon compounds involve large amounts of species and reactions. Even though the chemistry of hydrocarbon auto-oxidation has been studied extensively, no detailed kinetics has been established. Only a lumped two-step chemical

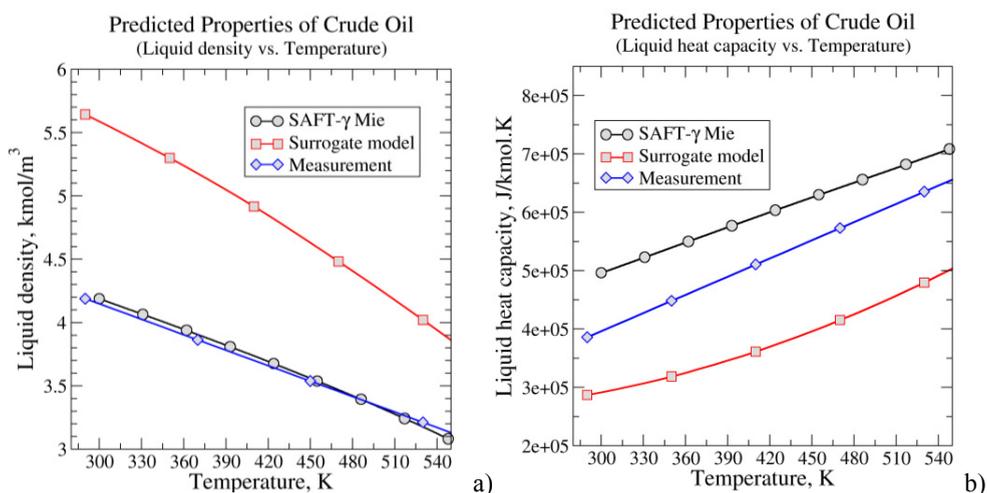
reaction scheme derived from the measurement of indene oxidation has been proposed to describe the chemical fouling process in crude oil^{2,8,9}. Clearly, the knowledge of chemical reaction fouling still remains its embryonic stage and requires more effort to address; this is beyond the scope of the present work.

The aim of the work presented herein is to study the non-isothermal flow dynamics of fouling in a closed-end heat-exchanger driven by chemical reactions and precipitation with a focus on elucidating the interaction between the two routes. The thermophysical properties and the phase behavior of an asphaltene-containing crude oil are estimate by using the SAFT- γ Mie theory¹⁰. The predicted physical properties and phase equilibria are incorporated within a computational fluid dynamics framework that permits the simulation of the fouling process. The simulation results are analyzed yielding insights into how the interaction between the two fouling routes can influence the overall fouling rate.

2. Numerical Models

2.1. Thermophysical properties

Crude oils are complex mixtures of hundreds of individual hydrocarbon compounds plus small quantities of impurities (primarily sulfur, nitrogen, oxygen, and some metals) and the actual compositions diff widely among locations. The crude oil properties can therefore vary significantly. In this study, a simple crude oil system comprising five alkane chain molecules was considered in which C_{13-17} , C_{17} , C_{18} , C_{19} and C_{20+} were selected in volumetric proportions of 69.5:17.1:8.4:3.9:1.1% according to the gas oil composition. The density and heat capacity were then calculated using SAFT- γ Mie EOS theory that employs the coarse-grained molecular modelling approach to describe fluids. The thermal conductivity and viscosity was predicted using the SuperTRAPP method due to its reliability and accuracy for oil and gas applications. The predicted properties were plotted and compared to those of mixing rule-based surrogate models and measured data from a UK refinery at temperatures of 300–560K. As shown in Fig. 1, the density predicted by the SAFT- γ method matches the measured data very well. The SAFT and SuperTRAPP also provide better predictions of the heat capacity, viscosity and thermal conductivity in comparison to surrogate models. The properties of heaviest molecule (C_{20+}) in the crude oil model were chosen to represent those of asphaltene.



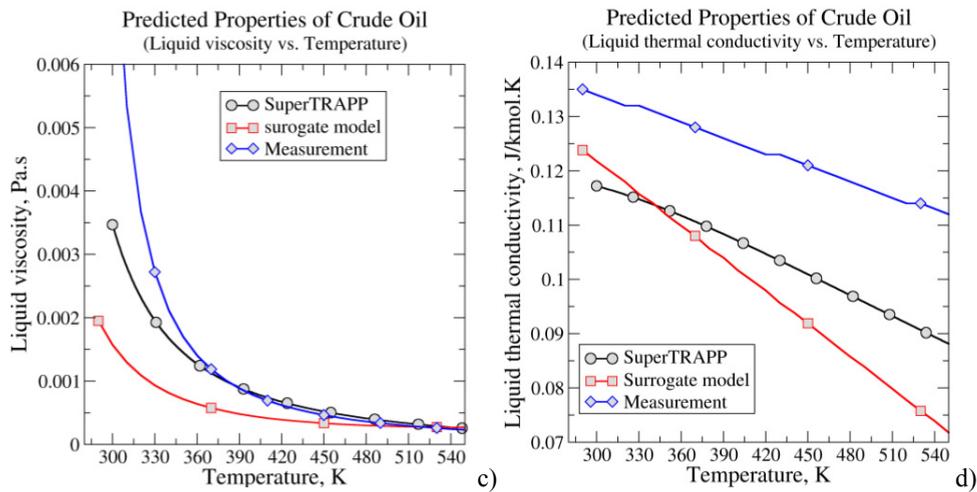


Fig. 1. Comparison of thermophysical properties of crude oil predicted by the SAFT- γ /SuperTRAPP, surrogate models, and measurement

2.2. Asphaltene Precipitation Model

Different SAFT models have been developed to study the molecular-thermodynamic of asphaltene-oil equilibria. Wu et al.⁶ proposed the McMillan–Mayer–SAFT EOS to predict the asphaltene solubility in different solvents and observed that raising the temperature decreases the solubility in propane diluents, and increases it in n-heptane diluents. The molecular parameters in the McMillan–Mayer–SAFT model must be adjusted according to measurements, which is costly. In addition, asphaltene is treated as an associating fluid in which hydrogen bonds tend to break easily at high temperature and the fluid becomes very soluble. Artola et al.⁷ explored the phase envelope of asphaltene-containing crude oil system using a more robust SAFT-VR model in which the intermolecular interaction was considered and polystyrene was selected to represent the asphaltene. Other SAFT-based methods have also been applied with some success in modelling the precipitation onset of asphaltene-containing fluid. Their accuracy, however, is largely dependent on the experimentally adjusted molecular parameters. To reduce the dependency on experimental data, the latest SAFT- γ Mie, a reformulation of the SAFT-VR Mie theory within a group contribution (GC) formalism, has been developed.

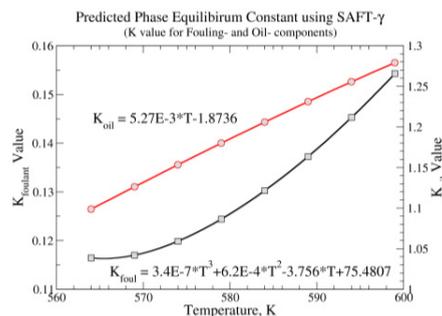


Fig. 2. Predicted phase equilibrium constant, K , and its correlation as a function of temperature.

In the present work, the SAFT- γ Mie method has been employed to predict the phase equilibrium constant, K , of a binary (asphaltene and oil) mixture. As shown in Fig. 2, the light oil components tend to migrate to the low-density phase as the temperature increases. As can be seen, K (with $K > 1$) for light hydrocarbon components increases with temperature, indicating that they are more volatile. Since the solvent leaves the high-density phase,

this gives the effect of higher fraction of asphaltene in this phase. Therefore, the fraction of asphaltene increases with temperature. The value of K being less than unity for asphaltene indicates that the compound is less volatile than the light hydrocarbons. The correlation of K with temperature has been fitted to estimate the mass flux, J , from the oil to the asphaltene phase.

It is assumed that J follows Fick's law of diffusion^{11,12}:

$$J = D_d \left(\frac{\rho \eta}{T} \frac{\partial T}{\partial n} \right) \quad (1)$$

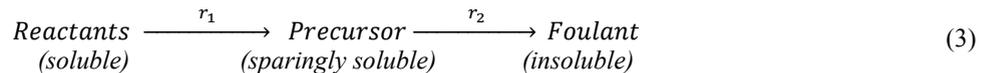
where the dimensionless parameter η has the following form:

$$\eta = \sum_{i=1}^n \eta_i, \quad \text{and} \quad \eta_i = \chi_i \frac{[T(1+\theta)^2 \frac{\partial L_x}{\partial T} + \theta \frac{\Delta H_{Pi}}{RT}] K_i}{(1+\theta K_i)^2} \quad (2)$$

The formulations for χ_i , θ and L_x are given and discussed elsewhere in the literature.

2.3. Chemical Reaction Fouling Model

The oxidation and auto-oxidation of light hydrocarbons, e.g. indene and kerosene-type fuels, have been widely studied and their kinetics can be applied to crude oil fouling. In general, the auto-oxidation is initiated by hydrogen atom abstraction caused by collisions between oil molecules and small radicals. The presence of oxygen allows hydrocarbon radicals to form hydroperoxide and polyperoxide which are finally converted into foulant species via the vinyl polymerization. This general auto-oxidation scheme was further lumped into two-step reactions⁸: the initial generation of a soluble precursor followed by the formation of an insoluble foulant as shown below:



Here, r_1 and r_2 are the reaction rates for the first and second reactions:

$$r_1 = k_1 C_{r1}^m C_{r2}^n \quad \text{and} \quad r_2 = k_2 C_p^l \quad (4)$$

In the above expressions, C_{r1} , C_{r2} and C_p are the concentration of reactants and precursor respectively; m , n , l are the orders of the reactants and precursors, respectively; k_1 and k_2 are reaction rate constants.

The reaction rates of indene oxidation have been derived for Russell's⁹ experiments in which the oxidation was performed in a closed, shaken flask at atmospheric and reduced pressures. These reaction rates have been further validated against the higher pressure (~ 4 bar) laboratory scale fouling apparatus in which the fouling resistance and deposition rate were measured for the heating tube filled with loop indene/kerosene fluids⁸. In our previous work^{3,4}, the pressure effect on the reaction rate was neglected and the reaction kinetics developed for low-pressure conditions was applied to predict the fouling at high operating pressure without any adjustments. Recent studies, however, revealed that the asphaltene oxidation has a strong pressure dependence¹³: the reaction rate increases with pressure. The maximum increase in reaction rate can reach 70% when the pressure increases from 4 bar to 20 bar at temperature ~ 370 K. Hence, the reaction rate constants have the following Arrhenius-type form:

$$k = A' \exp\left(-\frac{E_{act}}{RT}\right) \quad (5)$$

where A' is the pre-exponential factor, E_{act} is the activation energy, R is the gas constant, and T is the temperature. A' and E_{act} are the pressure-dependent parameter correlated from the measured value using below equations

$$A' = 0.0189 \exp(0.356 E_{act}) \quad \text{and} \quad E_{act} = [11.3 \ln(P) + 5.19] + 134.6 \frac{C7}{C5} \quad (6)$$

The asphalt compositional parameter ($C7/C5$) defined as the ratio of heptane asphaltenes ($C7$) to pentane asphaltenes ($C5$) takes the value of 0.526 in this work.

3. Fluid Dynamic Modeling of Crude Oil Fouling

In our previous work^{3,4}, a comprehensive model including the liquid properties, different fouling routes, as well as deposit ageing, has been implemented in a CFD tool to investigate the fouling formation and removal rate in turbulent flow in an open-end heat exchanger, under various operating conditions (flow rates and wall temperatures). It was found that different routes interact with each other, e.g. chemical reaction route was suppressed while the precipitation route was enhanced. The level of interaction level was shown to increase with wall temperature and to decrease with flow rate. To exclude the effect of turbulence and isolate the effects associated with the possible interaction between the different fouling routes, a closed-end heat exchanger filled with asphaltene-containing crude oil was modelled in the present study. In this case, laminar flow arises due to local movement driven by gravity, momentum transfer between phases, and natural convection. The Navier-Stokes equations together with the phase fraction function, and the energy equation are solved numerically in a single 3D tube 0.02×0.5 m ($D \times L$) with a constant wall temperature 575 K and initial oil temperature 475 K, using a commercial CFD package, ANSYS Fluent¹⁴. The Volume-of-Fluid (VOF) model was incorporated into the current CFD simulation to capture the interface between oil phase and fouling phase. Three different cases, corresponding to chemical route, precipitation route and combined route, were tested with the same initial conditions.

The time history of deposited asphaltene via different routes is shown in Fig 3a. The chemical reaction route produces about 7~8 times more asphaltene deposit than the precipitation route. This can be understood by comparing the mass transfer rate due to the different routes (see Fig 3b). The “pure” chemical route (i.e. fouling via chemical reactions solely) has a production rate around 4 times higher than the “pure” precipitation route. When combined with precipitation route, the chemical fouling rate slightly increased by ~4%, and precipitation rate decreased by ~50%. However, the overall fouling rate is still seen to increase somewhat. The enhancement and suppression of the chemical and precipitation routes is the opposite trend to that observed in our previous work. In the latter, turbulence as well as the endothermic/exothermic nature of the chemical reaction and precipitation routes were considered. The mass integral of species (soluble asphaltene and oil components) fraction in crude oil is plotted in Figs 3c-d. As shown, the reduction of soluble asphaltene concentration indicates fouling formation via different routes.

To gain in-depth understanding of the interaction between the two fouling routes, the iso-surface of asphaltene phase, fouling rate and temperature contours are shown in Fig 5. As can be seen, a large amount of asphaltene formed through the combined route and the chemical route solely adheres to the wall and accumulates at the bottom of the heat-exchanger due to gravity. The fouling layer, which has a higher thermal conductivity and specific heat capacity than the crude oil promotes heat transfer from the hot walls; this, in addition to heating the fluid in the heat-exchanger, leads to ‘hot spots’ in the asphaltene-oil mixture and large temperature gradients near the wall. The latter promote precipitation fouling in this region, which is to be expected by inspection of Eq. (1), since the precipitation flux J is proportional to the local temperature gradient. The increase in heat transfer rate from the walls leads to an increase in the rate of chemical reaction-driven fouling throughout the tube. This, then, leads to a concomitant rise in the rate of chemical fouling at the expense of the precipitation route. The overall increase in the fouling rate due to the combined, chemical and precipitation routes, leads to the formation of thick fouling deposits that accumulate near the wall (not shown), which then act to reverse the increase in heat transfer efficiency observed at early times.

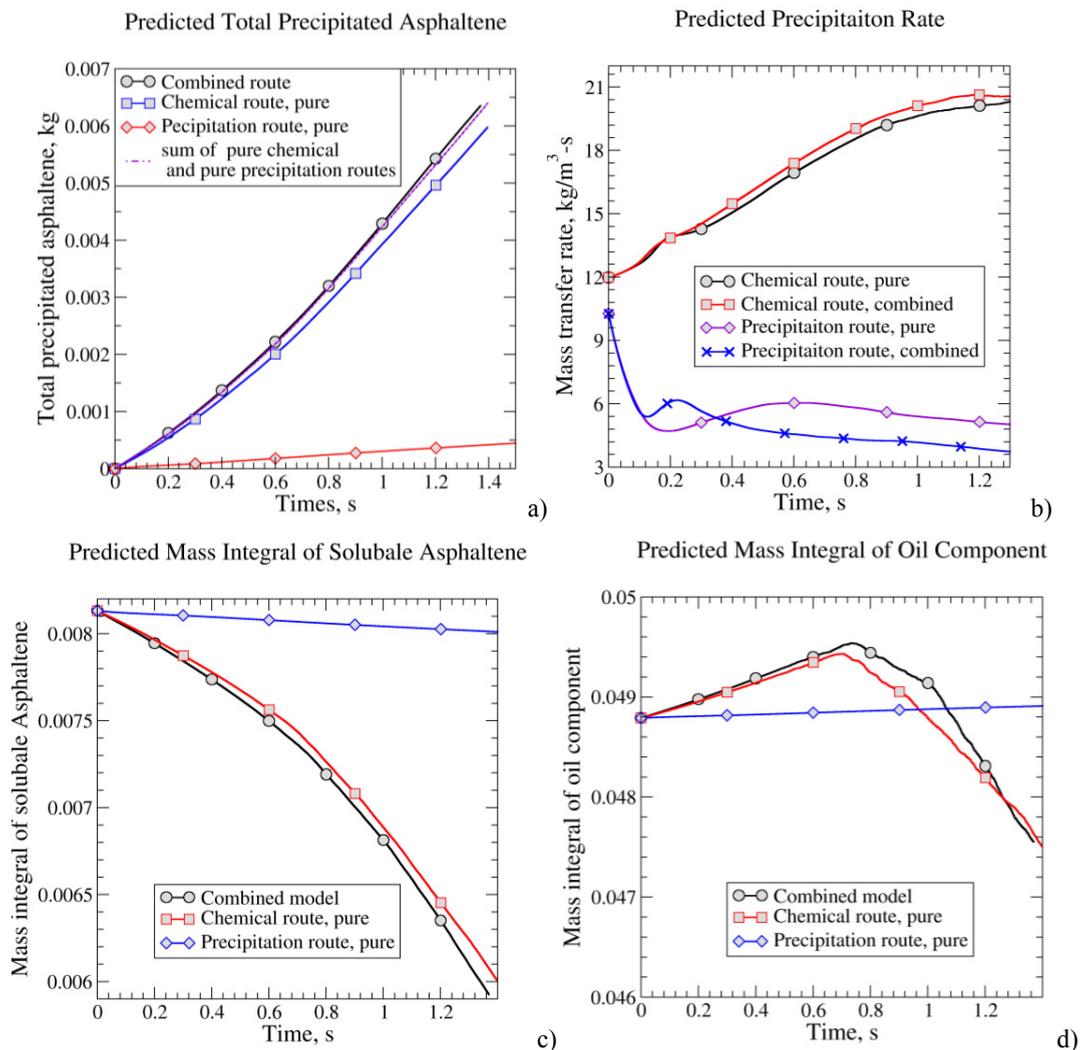


Fig. 3. Predicted time history of total mass of insoluble asphaltene, fouling rate, mass integral of oil component and soluble asphaltene component.

		iso-surface of the deposited asphaltene phase	Temperature and fouling rate
$T_{wall} = 575\text{ K}$ $T_{ini} = 475\text{ K}$	Combined chemical and precipitation-driven fouling		
	Chemical reaction-driven fouling		

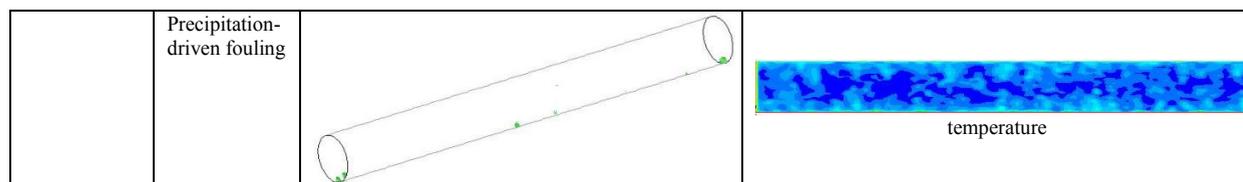


Fig. 4. Contour of iso-surface of insoluble asphaltene, temperature and fouling rate at time 1.4 s

4. Conclusion

The thermodynamic properties and phase equilibria of asphaltene-containing crude oil has been investigated using SAFT- γ Mie method. The temperature-dependent liquid properties of crude oil model have been predicted accurately compared to the measurement. The phase equilibrium constants have been calculated and fitted as a polynomial function of temperature. These thermodynamic properties together with a two-step chemical fouling scheme have been incorporated to the CFD to investigate the fouling process in a closed-end tube. The modeling results demonstrate the chemical route contributes more than 90% fouling formation. The chemical route tends to be enhanced slightly, albeit a large suppression for precipitation route, the total fouling formation still increases. The interaction between chemical route and precipitation route is due to the fouling layer formed adjacent to the wall. The fouling layer plays the role of thermal resistance, and thus hinders the heat transfer from hot wall surface to the cooler bulk fluid. This in turn induces a smaller temperature gradient in the fluid side. Consequently, the asphaltene precipitation was suppressed due to the insignificant temperature variation. On the other hand, the asphaltene has relatively higher thermal conductivity and heat capacity, which favor the thermal-absorbing effect and cause the locally hot zone adjacent to the wall. Accordingly, the chemical reaction fouling was enhanced by these locally high temperature zones.

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