2.0 Closed-Domain Hydrate Dissociation (Base Case w/ Hydrate)

2.1 Problem Description

One half of a 20-m, one-dimensional horizontal domain, discretized using uniformly spaced 1-m grid cells (optionally 0.1-m grid cells) is initialized with aqueous-hydrate conditions; whereas, the other half of the domain is initialized with gas-aqueous conditions. As with the Base Case problem, a closed horizontal domain is used to eliminate gravitational body forces and boundary condition effects. The initial conditions are specified to yield complete dissociation of the hydrate, via the thermal capacitance of the domain-half initialized with gas-aqueous conditions. To initialize the aqueous-hydrate half of the domain, temperature, pressure, and hydrate saturation are specified. For reference purpose hydrate equilibrium pressure, hydration number, and cage occupancies will also be specified for this half of the domain. To initialize the gas-aqueous half of the domain temperature, aqueous pressure and gas pressure are specified. All active phases (i.e., aqueous, gas, and hydrate) are assumed to comprise water and CH_4, and capillarity is assumed between the active phases. Hydrate dissociation is assumed to occur using equilibrium kinetics (i.e., infinitely fast dissociation rates). From the specified initial conditions, the simulations proceeds to equilibrium conditions in temperature and pressure, dissociating the hydrate during the transition process and leaving gas-aqueous conditions. Variable time stepping should be used to capture the flow and transport processes at early and late times during simulation. A schematic of the initial conditions for the problem are shown in Figure 2.1 and problem parameters and specifications are provided in Table 2.1. In Figure 2.1 the specified initial condition parameters are listed above the domain region and the computed initial condition parameters are listed for reference inside the domain region. The computed initial condition parameters are computable from the specified initial condition parameters.

The list of processes simulated in this problem include:

5. multifluid flow for an aqueous-gas-hydrate system in geological media, subject to relative permeability and capillarity effects and phase transitions
6. dissociation of CH_4 hydrate in response to thermal stimulation and depressurization
7. heat transport across multifluid geological media with phase advection and component diffusion
8. change in CH_4 solubility in water with pressure and temperature
9. change in thermodynamic and transport properties with pressure and temperature

2.2 Simulation Results

Profiles of temperature, aqueous saturation, hydrate saturation, gas saturation, aqueous pressure, and CH_4 mass fractions in the active phases at selected times (0, 1, 10, 100, 1,000, and 10,000 days) are shown in Figures 2.2 through 2.9, respectively. Each figure shows results from the 20- and 200-node discretizations. The profile plots show equilibrium conditions are achieved by 10,000 days. Complete hydrate dissociation

Table 2.1. Problem Parameters and Specifications

Parameter	Value
Porosity	0.3
Bulk Density	1855 kg/m^3
Grain Density	2650 kg/m^3
Bulk Specific Heat	525 J/kg K
Grain Specific Heat	750 J/kg K
Hydraulic Conductivity	0.1 Darcy
Dry Thermal Conductivity	2.0 W/m K
Water-Saturated Thermal Conductivity	2.18 W/m K
Pore Compressibility	5.0 x 10^{-10} Pa^{-1}
Capillary Pressure Model	van Genuchten, see Equation (1.1)
α parameter	0.132 m^{-1}
n parameter	2.823
β_{gl} parameter	1.0
s_{lr} parameter	0.0
Aqueous Relative Permeability Model	Mualem, see Equation (1.2)
m parameter	0.6458
Gas Relative Permeability Model	Mualem, see Equation (1.3)
m parameter	0.6458

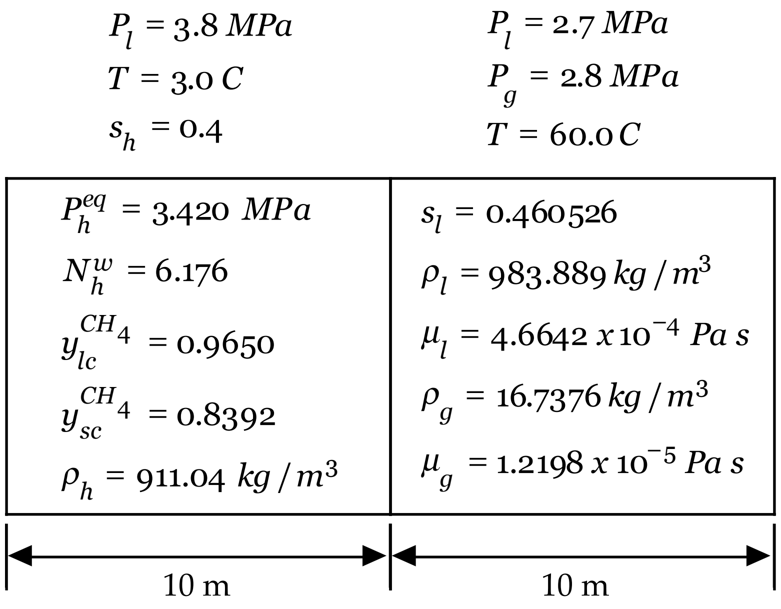

Figure 2.1. Problem Schematic

occurs by 1,924 days, after which time the thermal, thermodynamic, and hydrologic systems transition smoothly toward the equilibrium conditions shown in Table 2.1; where simulation results are shown for both the 20- and 200-node discretizations. Hydrate dissociation occurs initially in response to both thermal stimulation and depressurization; however, later in time dissociation is principally due to thermal stimulation as the released CH_4 gas increases the system pressure above the initial conditions. Initially hydrate dissociation occurs without hydrate creation. After 10 days, however, hydrate dissociation occurs in conjunction with hydrate creation on the hydrate-side of the dissociation front (Figure 2.4). Hydrate creation is caused by the released CH_4 gas migrating away from the dissociation region in both directions. CH_4 gas migrating toward the hydrate-side of the domain forms new hydrate, which eventually dissociates as the dissociation front proceeds toward the hydrate side of the domain. The total CH_4 mass remains unchanged during the simulation at 167.025 kg, indicating mass conservation of CH_4. The aqueous CH_4 concentration is generally dependent on CH_4 gas partial pressure, which increase over time with the increasing system pressure, as shown by the profiles in Figures 2.7 and 2.8. Integral and rates of CH_4 released from the hydrate are shown in Figure 2.9 as volumes at STP; where, the conversion from kg to m^3 STP was taken as 1.4706. Volumetric release rates were calculated by differentiating the released volumes.

To further illustrate the transition to equilibrium and dissociation of hydrate, history plots of temperature, aqueous saturation and hydrate saturation are shown at four domain locations (i.e., 0.5, 9.5, 11.5 and 19.5 m) in Figures 2.10 through 2.12, respectively. It should be noted that the temperature near the hydrate interface (i.e., x = 9.5 m) shows a drop below the initial condition (i.e., 3 C) early in the dissociation process for that node location (see Figure 2.10). This drop in temperature occurs in response to the dissociation of hydrate via depressurization, that leads the thermal stimulation dissociation. The complex history profiles for aqueous saturation, shown in Figure 2.11, occur in response to advective migration of the aqueous phase due to pressure gradients and the liberation of water with the dissociation of hydrate. The creation of hydrate on the hydrate-side of the domain, prior to dissociation is shown in Figure 2.12, at the domain location x = 0.5 m.

Table 2.2 Equilibrium Conditions

Parameter	20-Node Discretization	200-Node Discretization
Temperature	18.063 C	18.054 C
Aqueous Pressure	10.1736 MPa	10.1926 MPa
Gas Pressure	10.2428 MPa	10.2617 MPa
Aqueous Saturation	0.679	0.680
Hydrate Saturation	0.0	0.0
Aqueous Relative Permeability	0.1333	0.1338
Aqueous CH_4 Mass Fraction	2.162×10^{-3}	2.166×10^{-3}
Gas CH_4 Mass Fraction	0.99981	0.99981

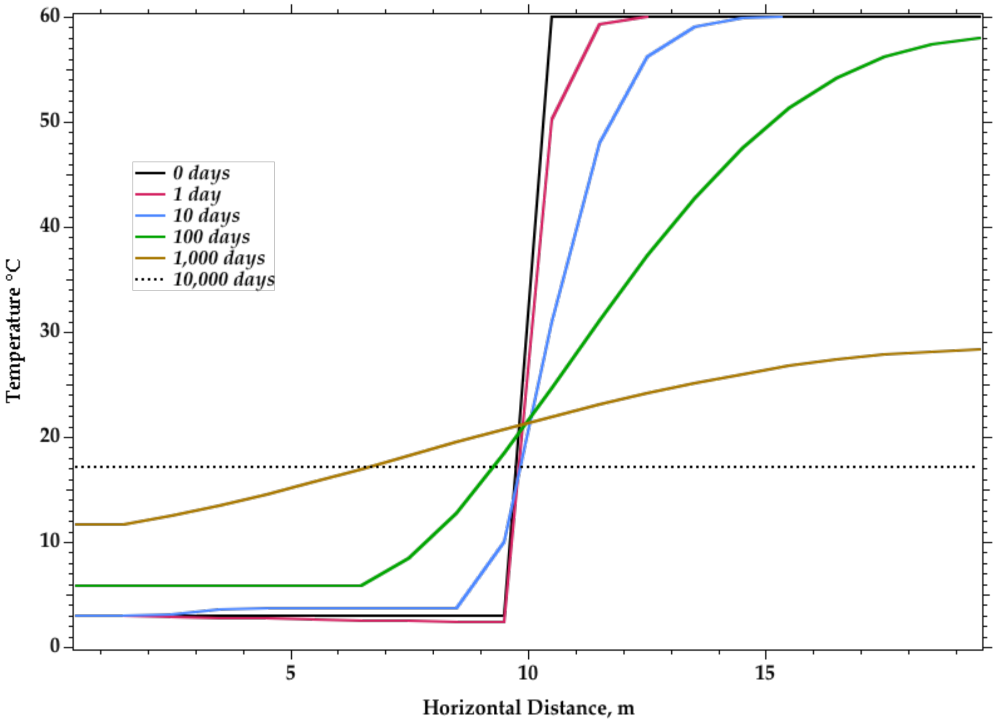

Figure 2.2a. Simulated Temperature Profiles (20-Node Discretization)

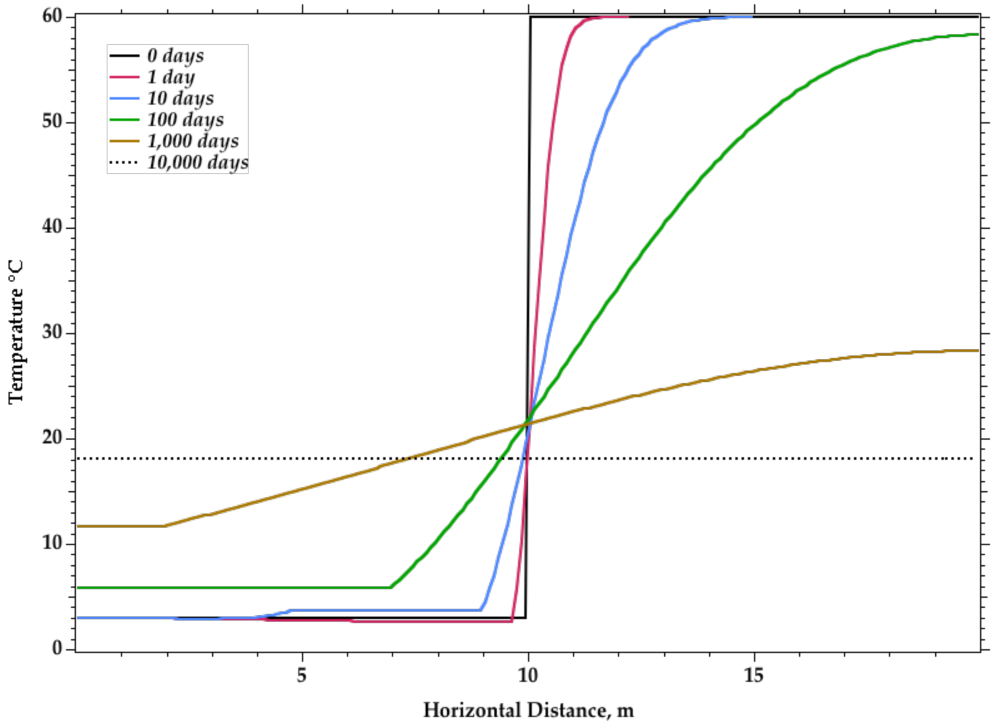

Figure 2.2b. Simulated Temperature Profiles (200-Node Discretization)

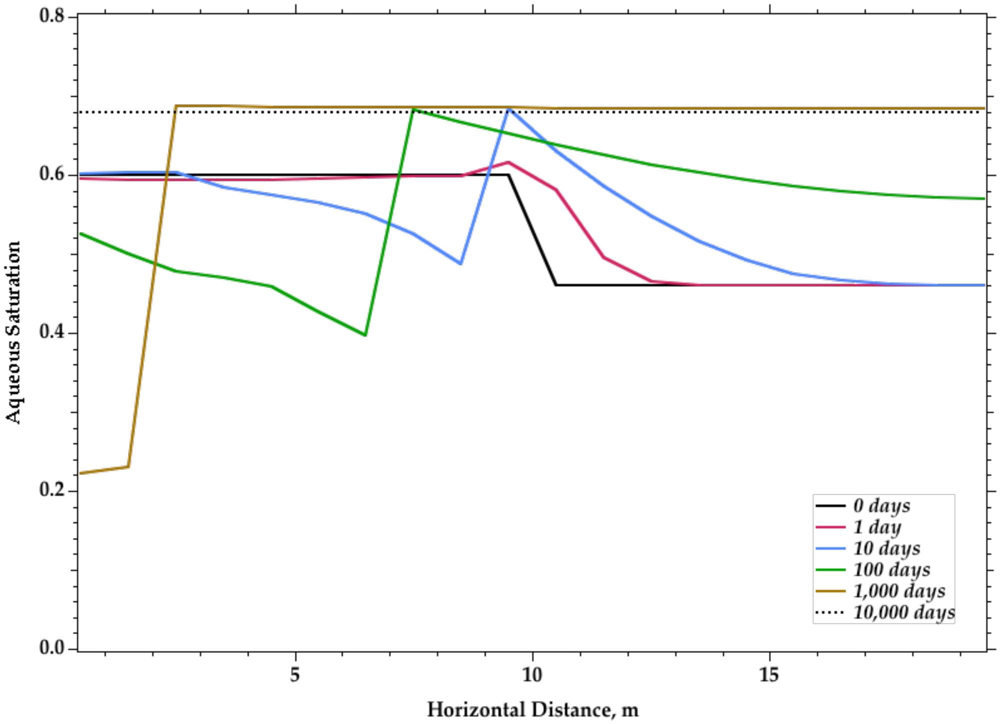

Figure 2.3a. Simulated Aqueous Saturation Profiles (20-Node Discretization)

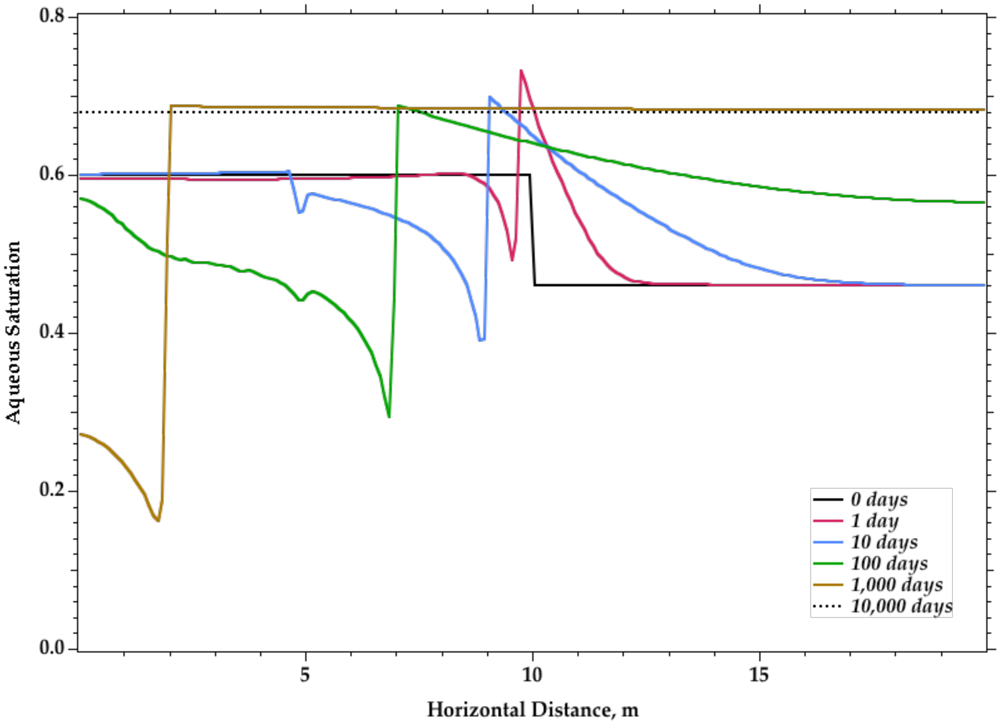

Figure 2.3b. Simulated Aqueous Saturation Profiles (200-Node Discretization)

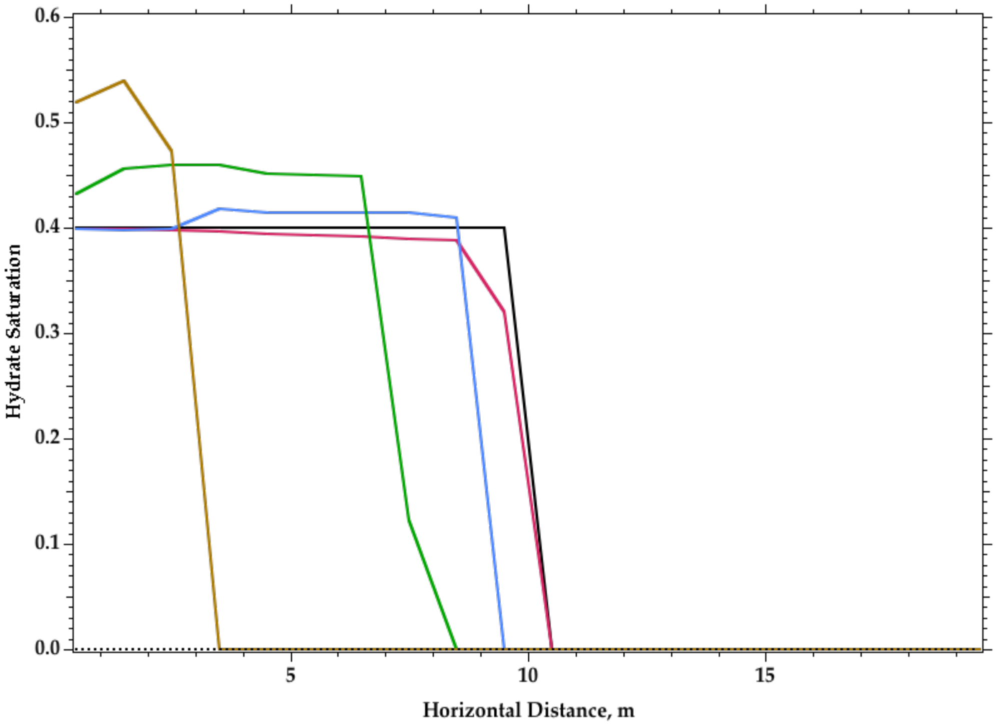

Figure 2.4a. Simulated Hydrate Saturation Profiles (20-Node Discretization)

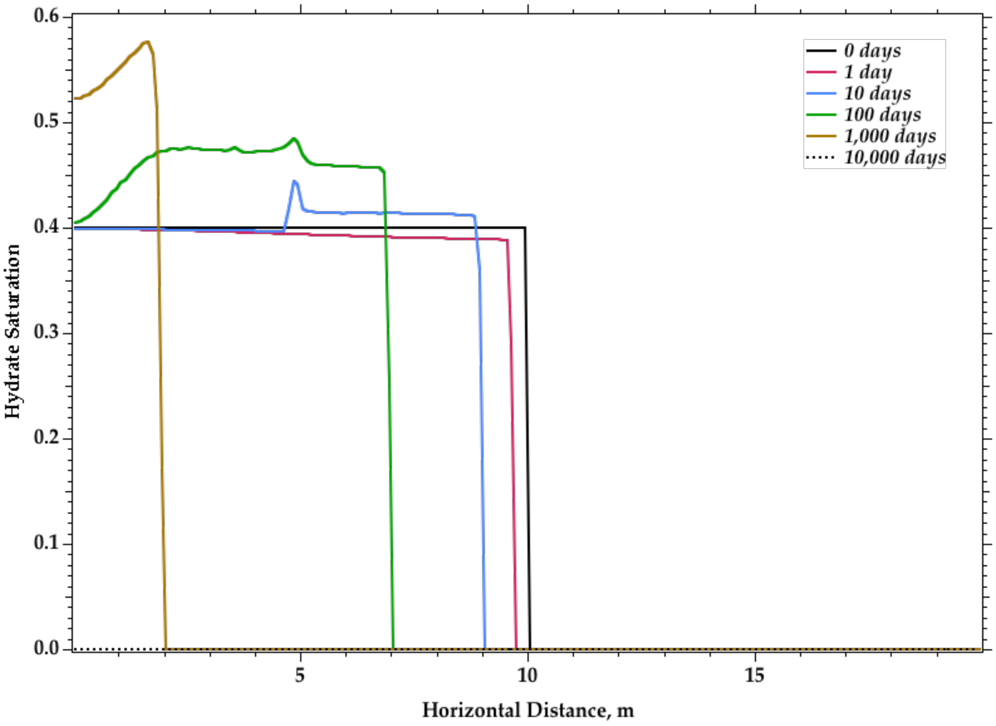

Figure 2.4b. Simulated Hydrate Saturation Profiles (200-Node Discretization)

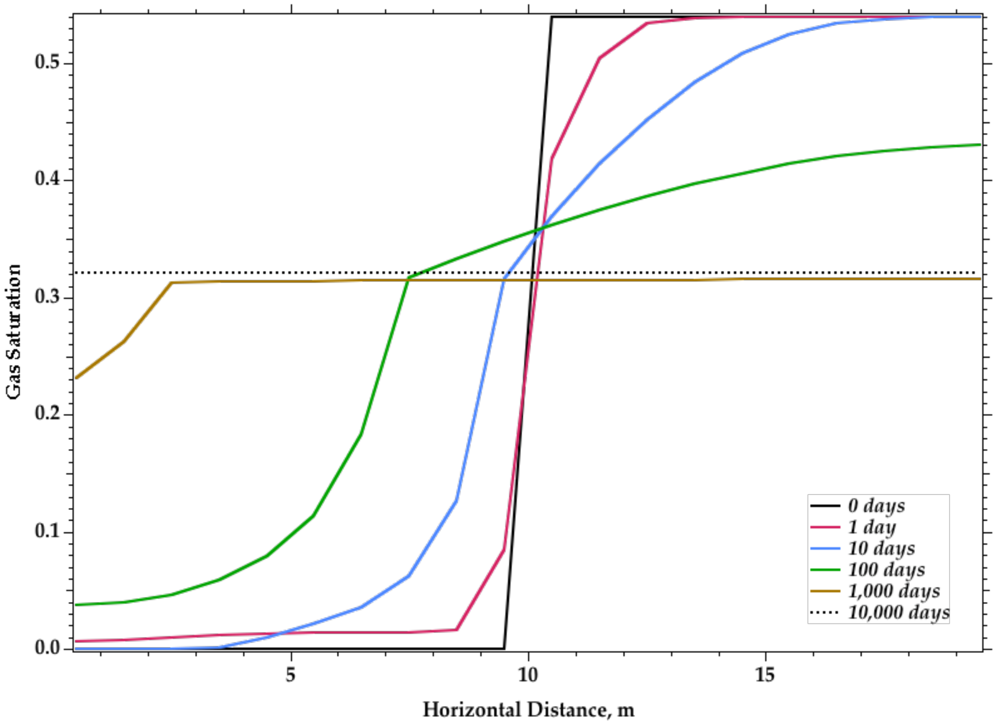

Figure 2.5a. Simulated Gas Saturation Profiles (20-Node Discretization)

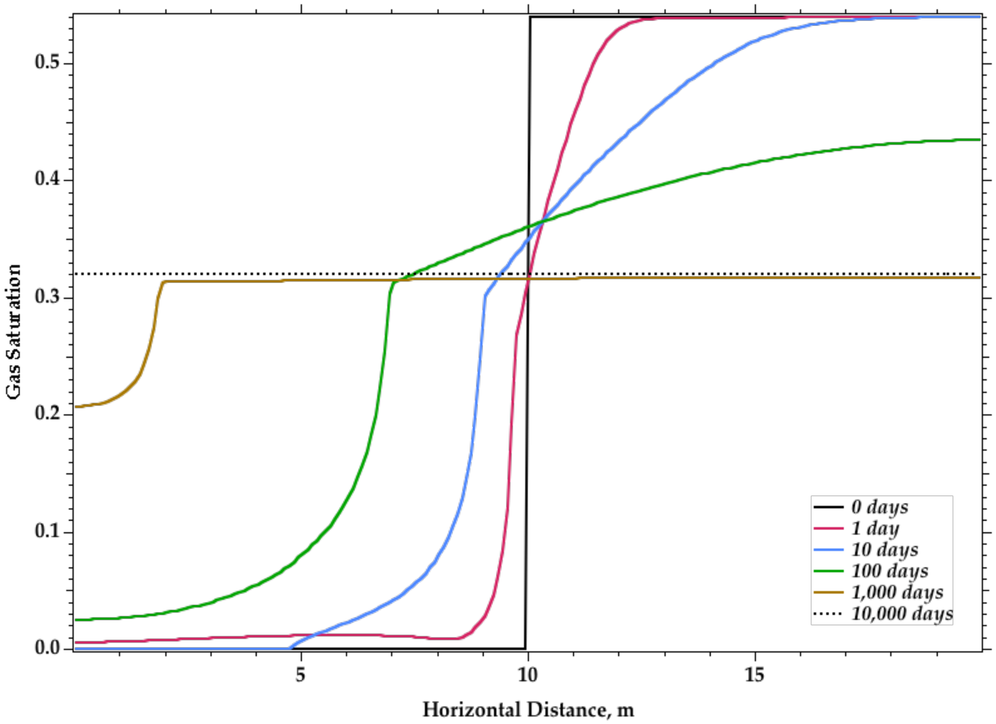

Figure 2.5b. Simulated Gas Saturation Profiles (200-Node Discretization)

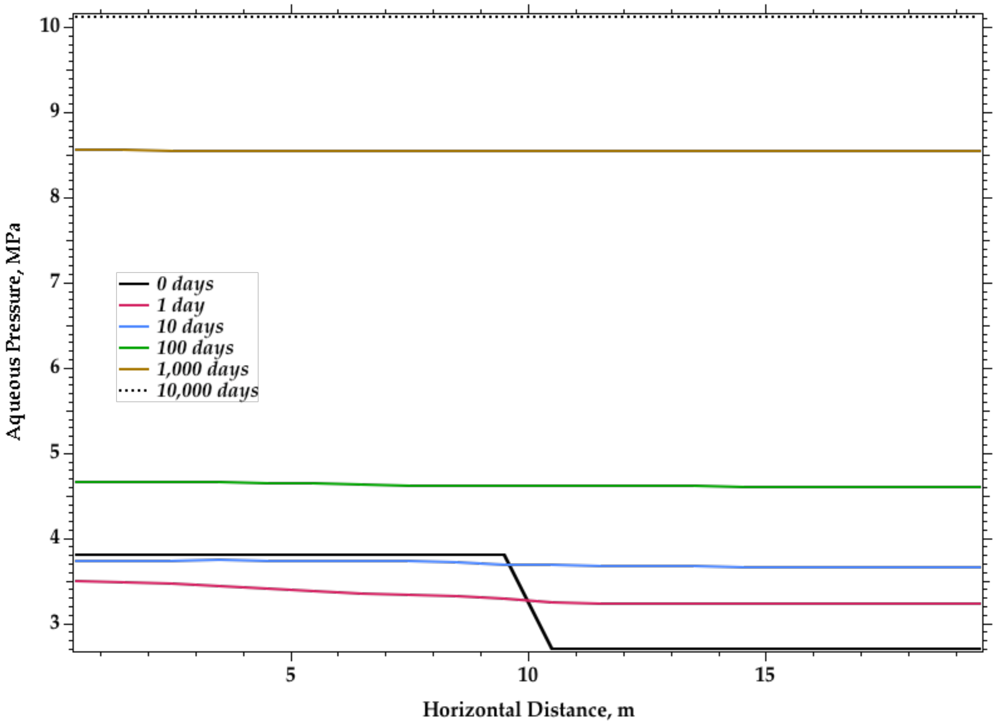

Figure 2.6a. Simulated Aqueous Pressure Profiles (20-Node Discretization)

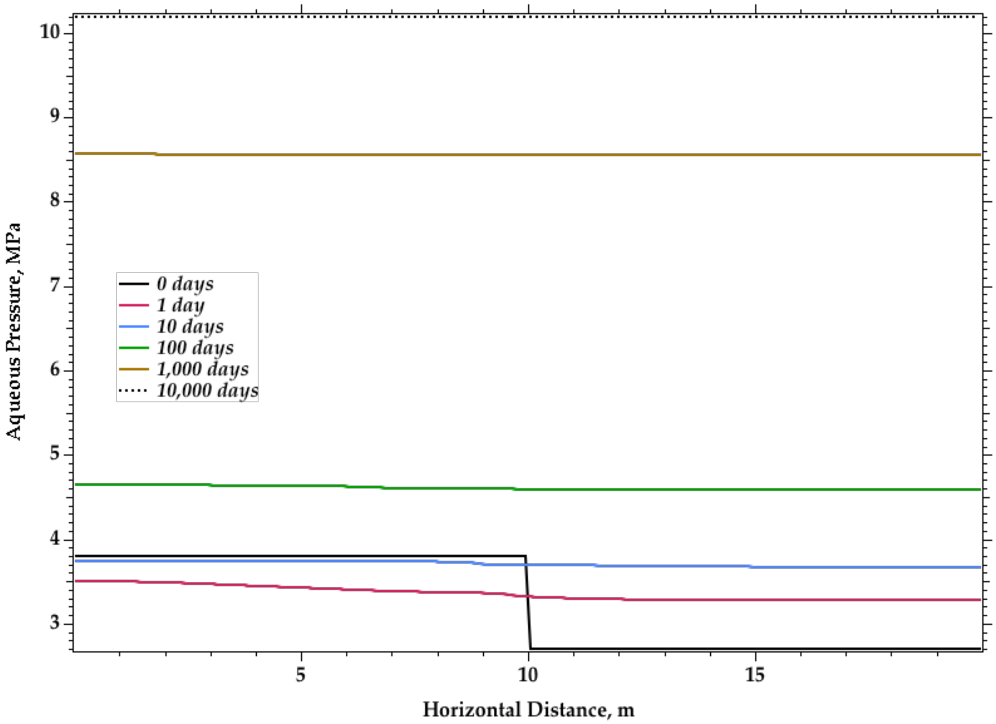

Figure 2.6b. Simulated Aqueous Pressure Profiles (200-Node Discretization)

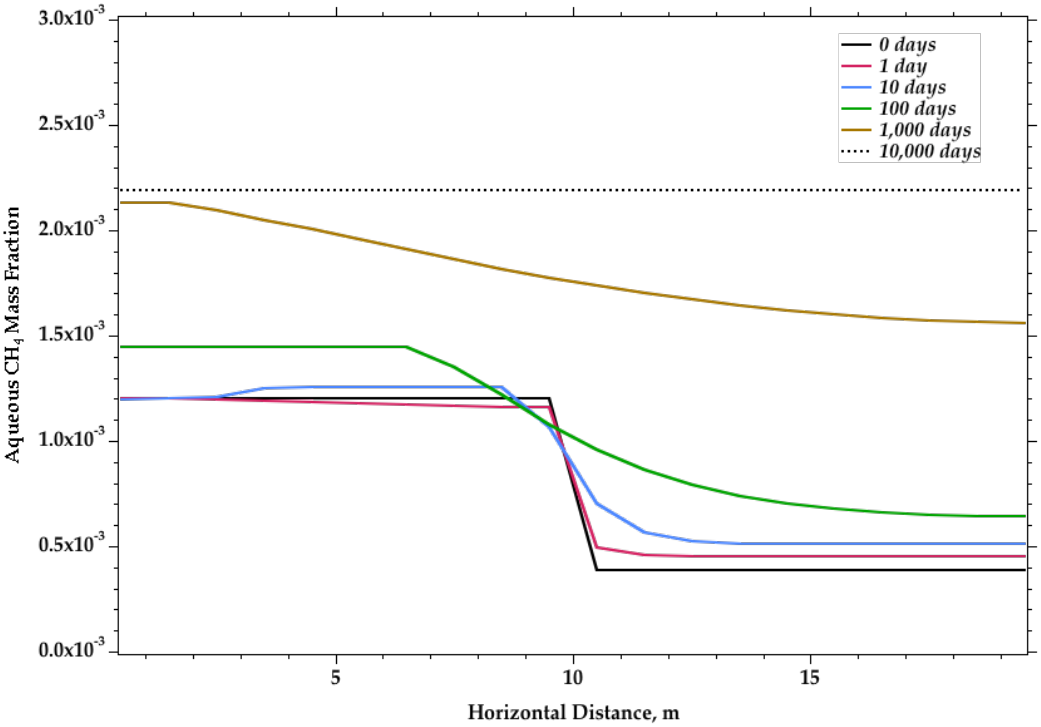

Figure 2.7a. Simulated Aqueous CH_4 Mass Fraction Profiles (20-Node Discretization)

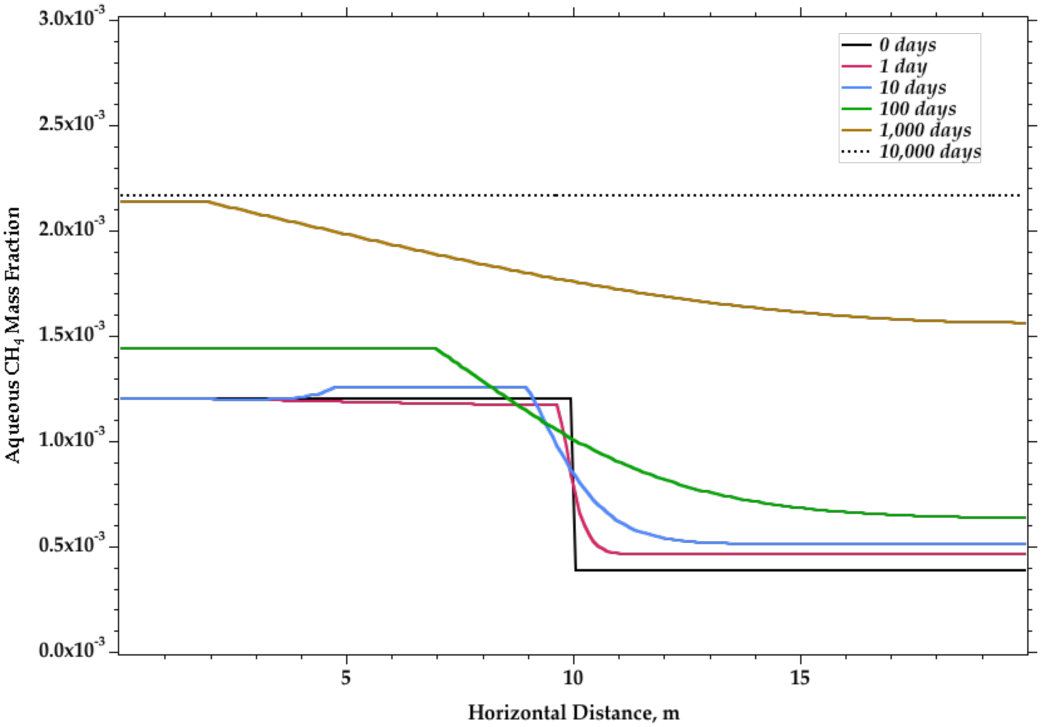

Figure 2.7b. Simulated Aqueous CH_4 Mass Fraction Profiles (200-Node Discretization)

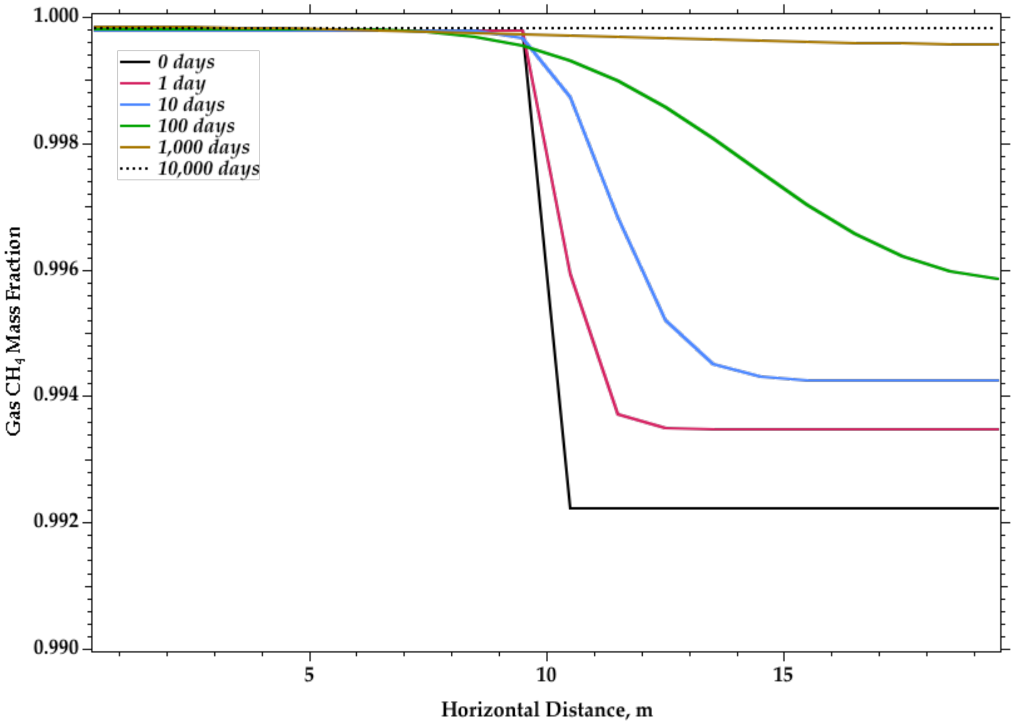

Figure 2.8a. Simulated Gas CH_4 Mass Fraction Profiles (20-Node Discretization)

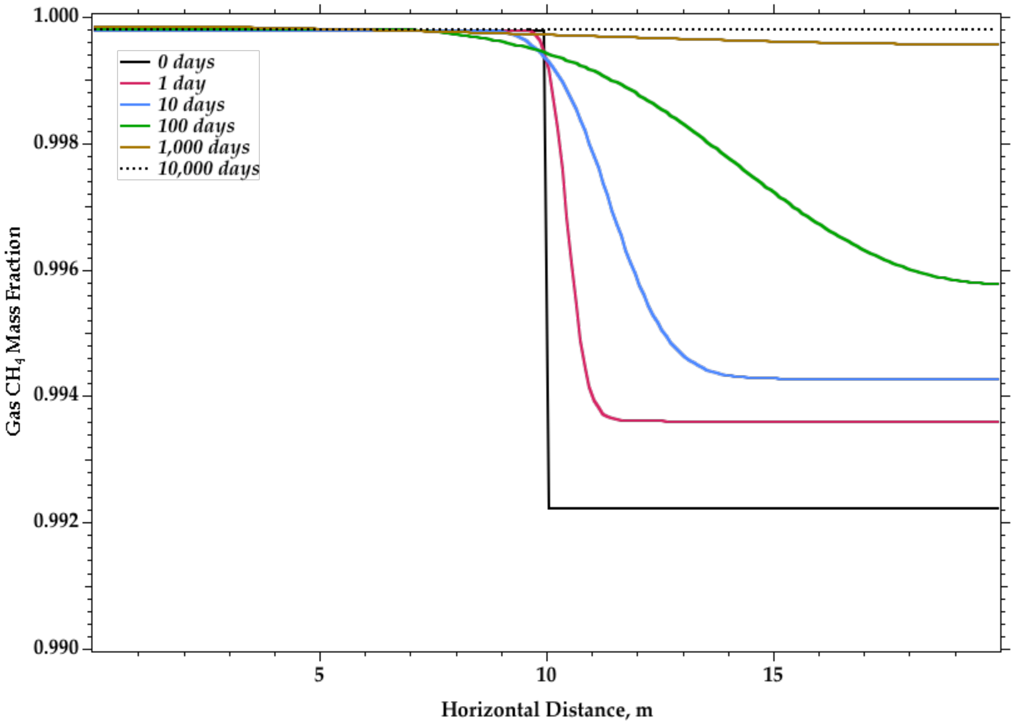

Figure 2.8b. Simulated Gas CH_4 Mass Fraction Profiles (200-Node Discretization)

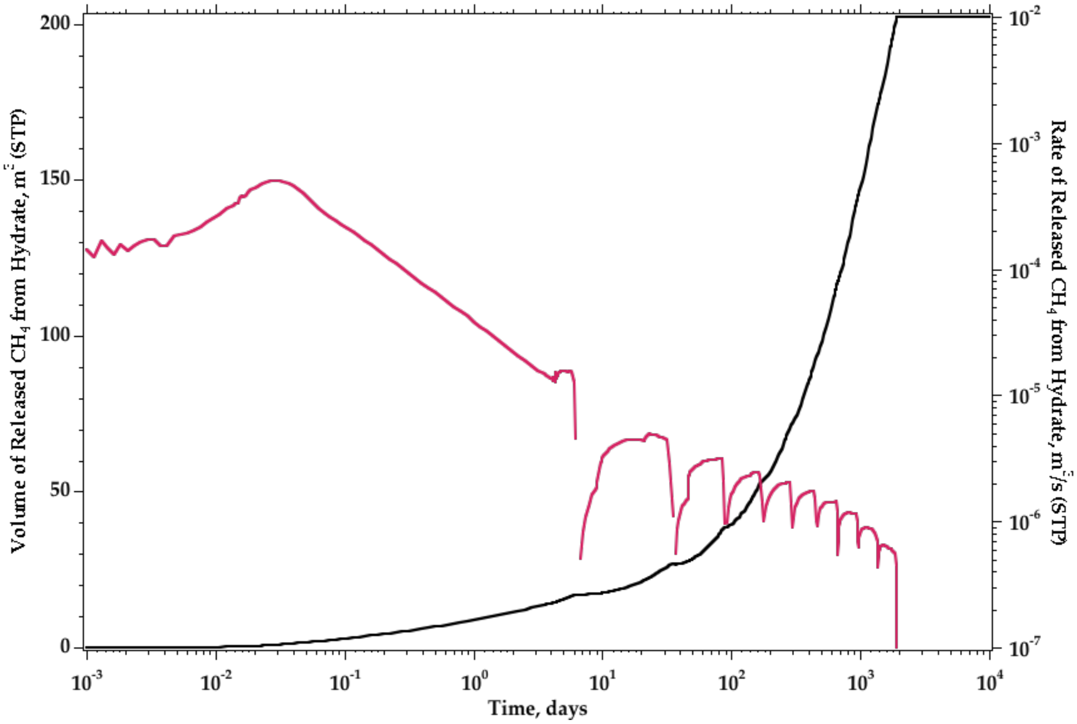

Figure 2.9a. Simulated CH_4 Release from Hydrate (20-Node Discretization)

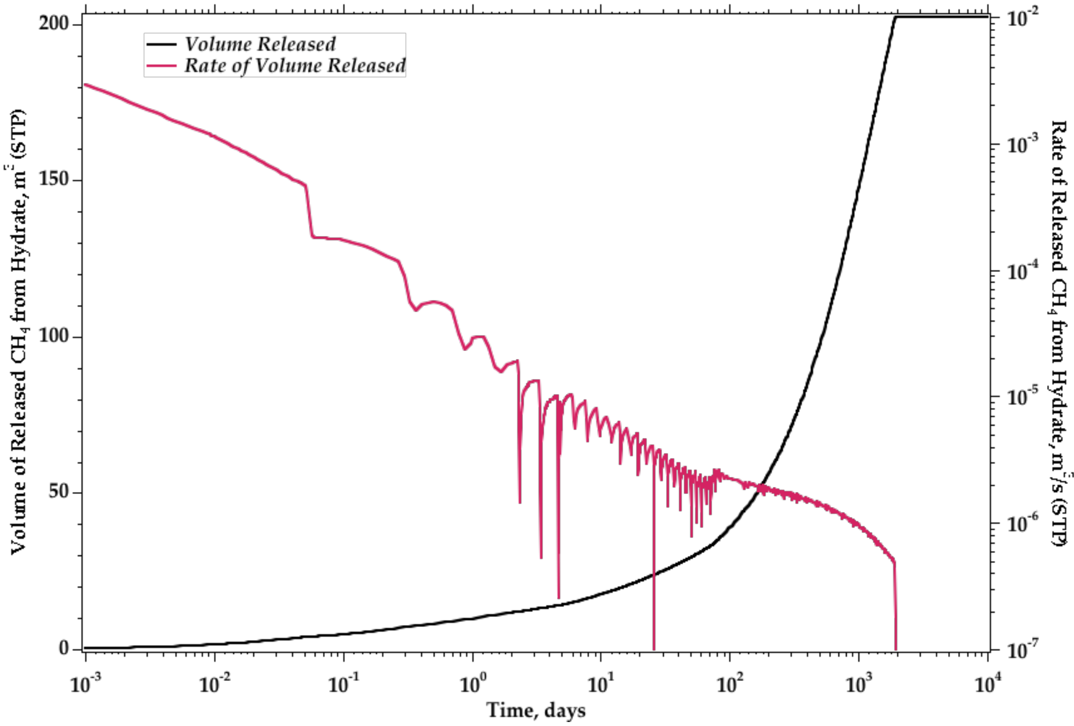

Figure 2.9b. Simulated CH_4 Release from Hydrate (200-Node Discretization)

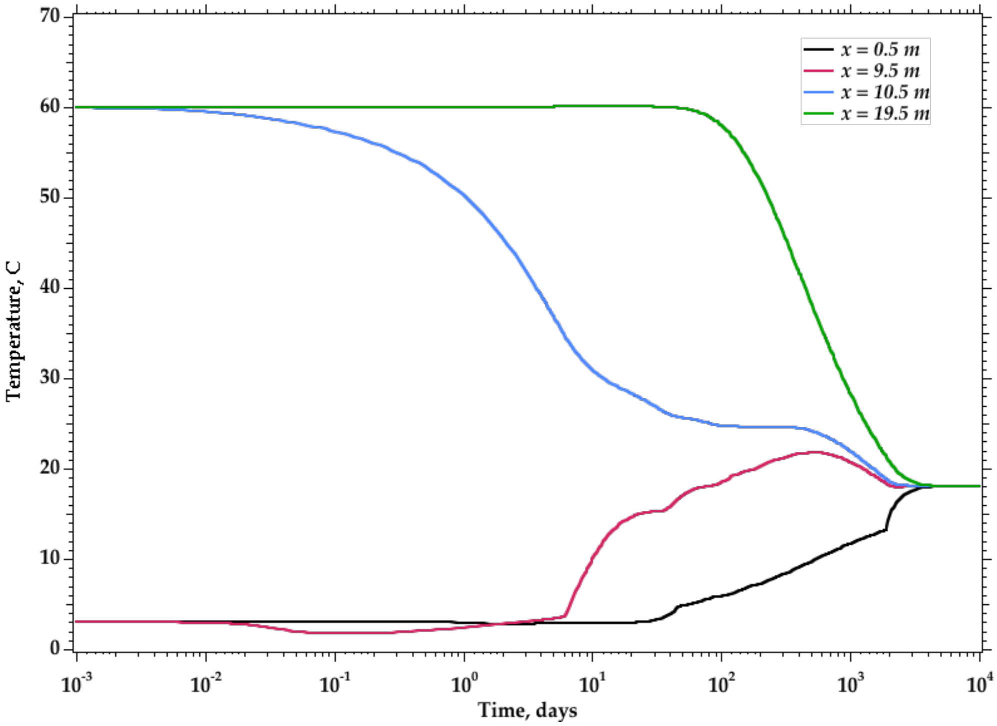

Figure 2.10a. Simulated Temperature History Profiles (20-Node Discretization)

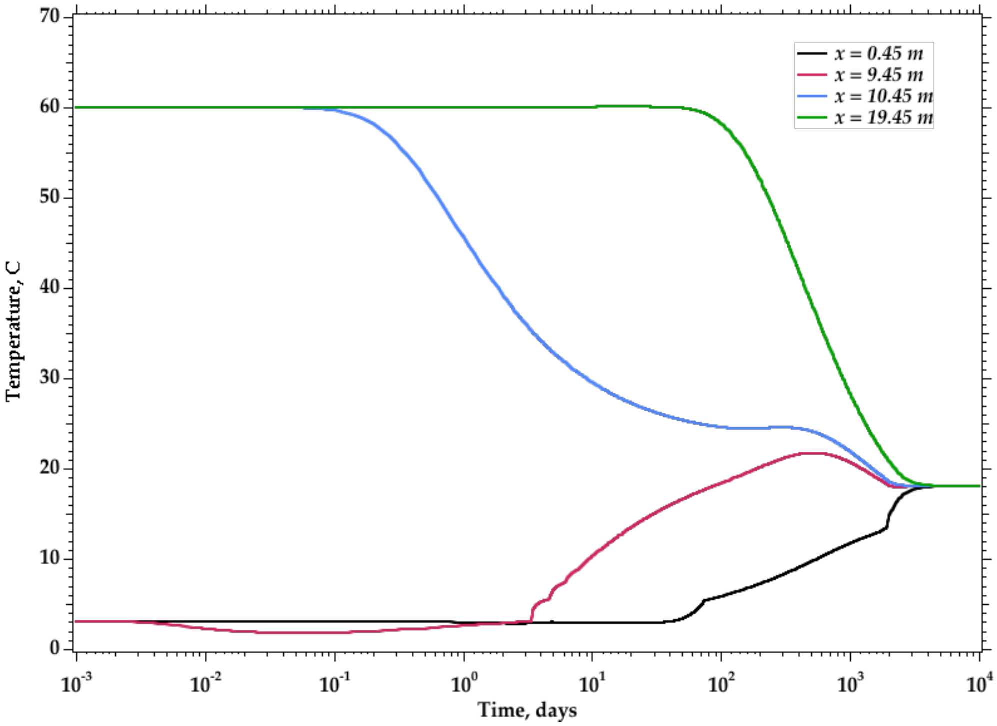

Figure 2.10b. Simulated Temperature History Profiles (200-Node Discretization)

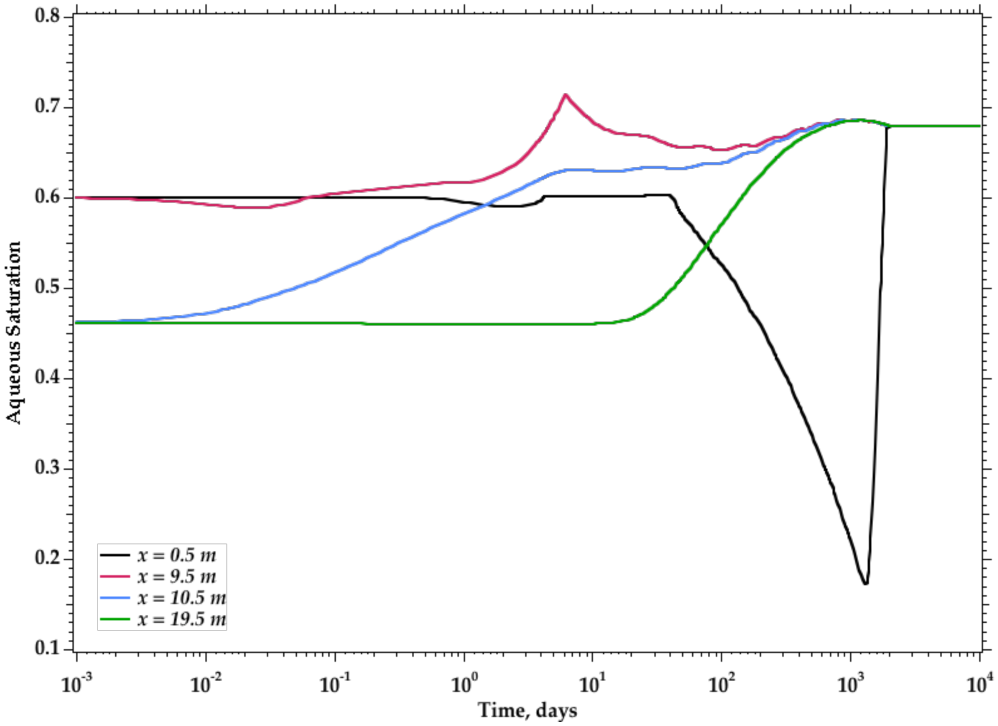

Figure 2.11a. Simulated Aqueous Saturation History Profiles (20-Node Discretization)

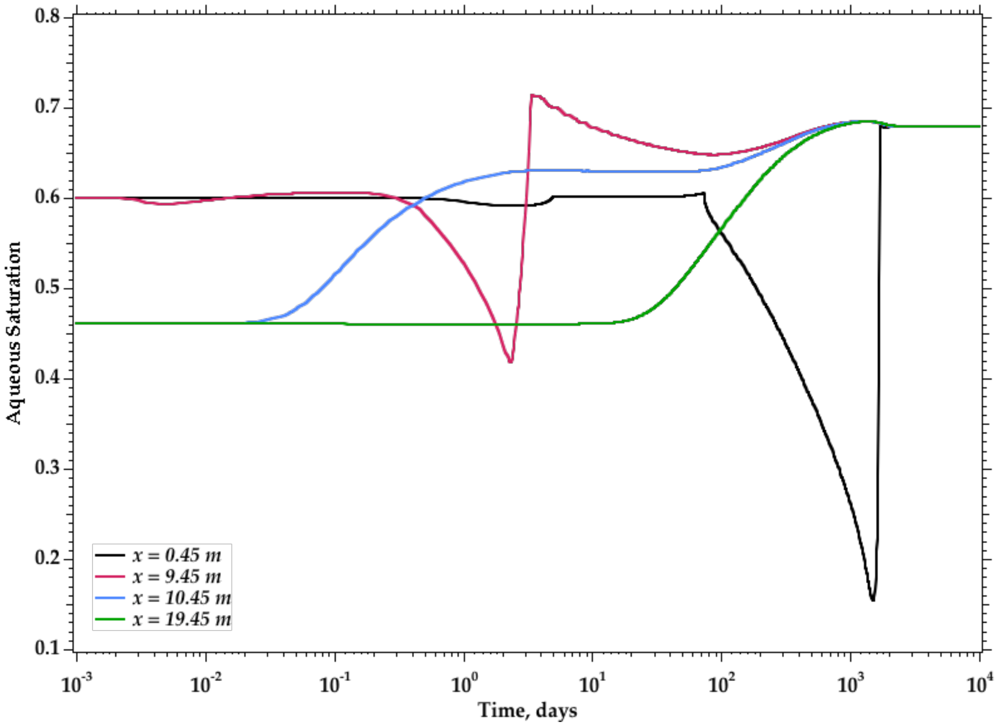

Figure 2.11b. Simulated Aqueous Saturation History Profiles (200-Node Discretization)

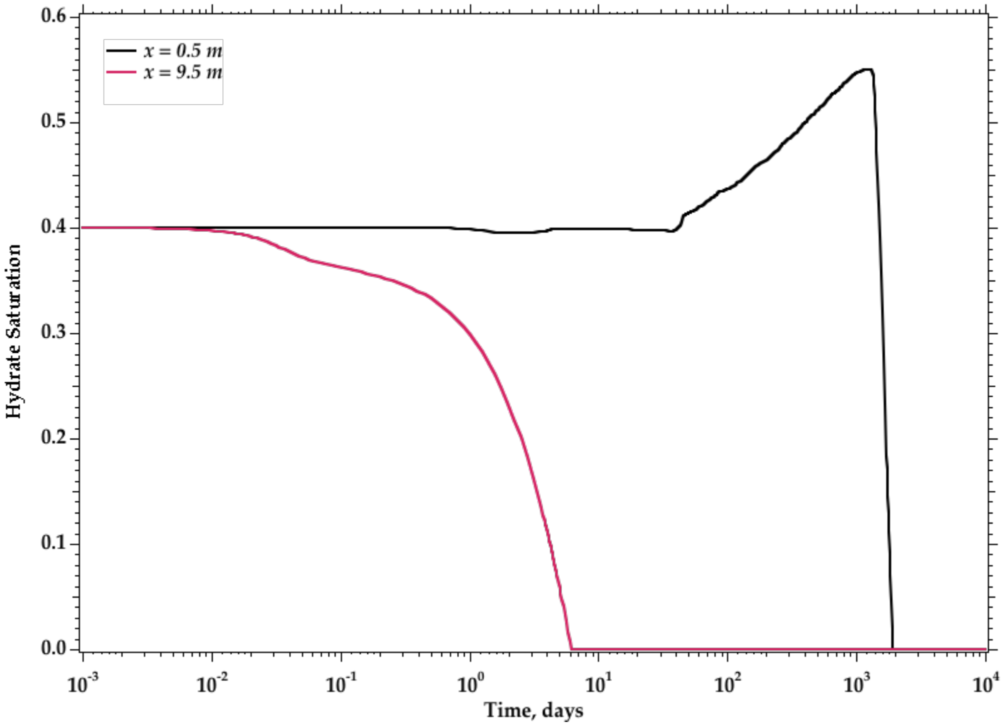

Figure 2.12a. Simulated Hydrate Saturation History Profiles (20-Node Discretization)

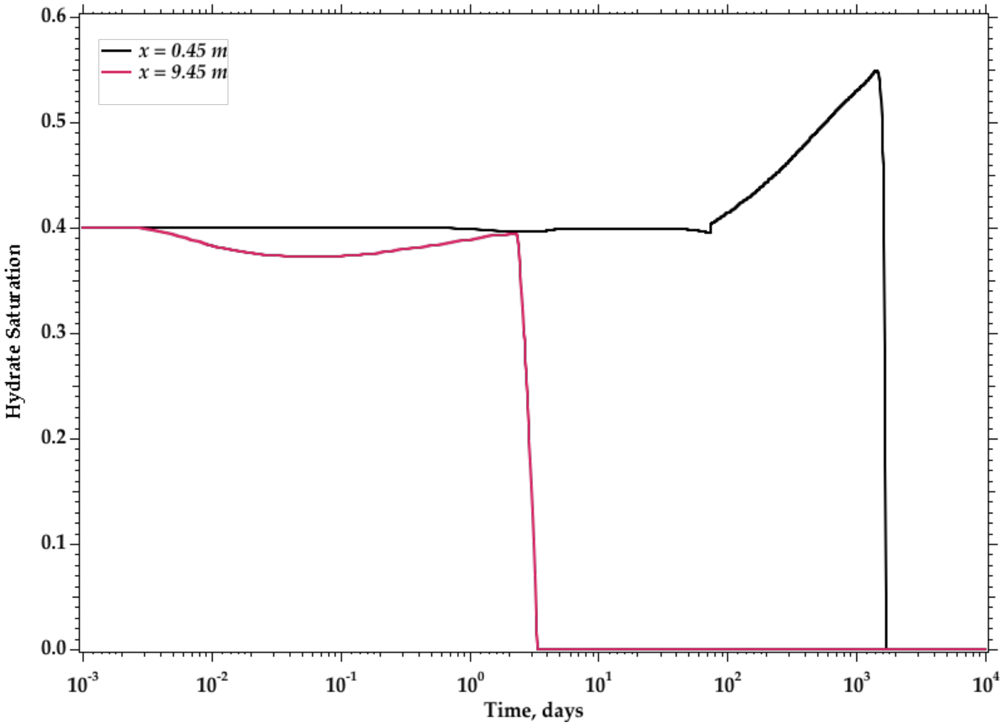

Figure 2.12b. Simulated Hydrate Saturation History Profiles (200-Node Discretization)

3.0 References

Mualem, Y. 1976. "A new model for predicting the hydraulic conductivity of unsaturated porous media." *Water Resources Research*. 12:513-522.

van Genuchten, M. T. A. 1980. "A closed-form equation for predicting the hydraulic conductivity of unsaturated soils." *Soil Sci. Soc. Am. J.* 44:892-898.

Appendix

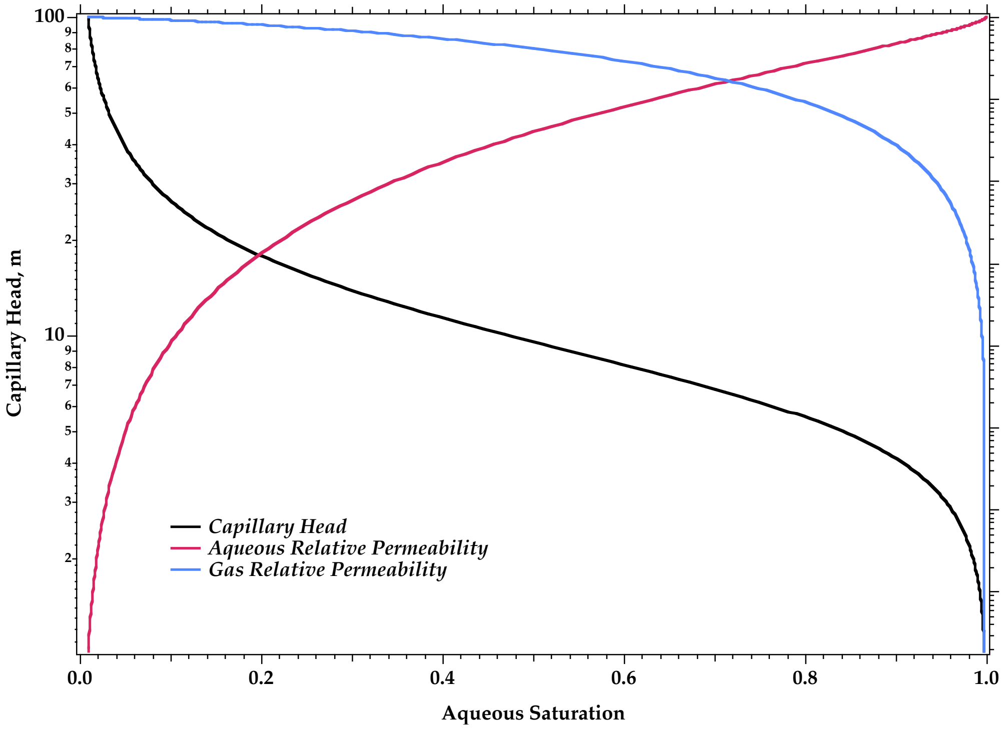

Figure A.1. van Genuchten and Mualem Functions

Table A.1 van Genuchten and Mualem Functions

Aqueous Saturation	Capillary Head, m	Aqu. Rel. Perm.	Gas Rel. Perm.
1	0	1	0
0.99777	1.01822	0.948178	3.12211e-05
0.997653	1.03678	0.946455	3.41961e-05
0.997531	1.05567	0.944675	3.74549e-05
0.997402	1.07491	0.942837	4.10224e-05
0.997267	1.0945	0.940938	4.49304e-05
0.997125	1.11445	0.938979	4.9208e-05
0.996975	1.13475	0.936955	5.38936e-05
0.996817	1.15543	0.934865	5.90233e-05
0.996651	1.17649	0.932708	6.46395e-05
0.996477	1.19793	0.93048	7.07881e-05
0.996294	1.21976	0.928181	7.75207e-05
0.996101	1.24199	0.925807	8.48929e-05
0.995898	1.26462	0.923357	9.29598e-05
0.995684	1.28767	0.920828	0.000101793
0.99546	1.31113	0.918218	0.000111461
0.995224	1.33503	0.915524	0.000122046
0.994976	1.35936	0.912745	0.000133629
0.994715	1.38413	0.909877	0.000146308
0.99444	1.40935	0.906917	0.000160183

0.994152	1.43504	0.903864	0.000175371
0.993848	1.46119	0.900714	0.000191988
0.993529	1.48782	0.897466	0.000210172
0.993194	1.51493	0.894115	0.000230066
0.992841	1.54254	0.89066	0.000251832
0.99247	1.57065	0.887097	0.000275644
0.99208	1.59927	0.883423	0.000301692
0.99167	1.62841	0.879635	0.000330188
0.991239	1.65809	0.875731	0.000361352
0.990786	1.68831	0.871707	0.000395431
0.99031	1.71907	0.86756	0.000432703
0.98981	1.7504	0.863287	0.000473452
0.989285	1.7823	0.858885	0.000518006
0.988732	1.81478	0.854351	0.00056671
0.988152	1.84785	0.84968	0.000619949
0.987542	1.88152	0.844871	0.000678132
0.986901	1.91581	0.83992	0.000741714
0.986228	1.95073	0.834823	0.000811186
0.985521	1.98627	0.829578	0.000887087
0.984778	2.02247	0.82418	0.000969995
0.983998	2.05933	0.818628	0.00106054
0.983179	2.09686	0.812916	0.00115942
0.982319	2.13507	0.807044	0.00126738
0.981416	2.17398	0.801006	0.00138522
0.980468	2.21359	0.794801	0.00151383
0.979473	2.25393	0.788425	0.00165418
0.978429	2.29501	0.781875	0.00180728
0.977333	2.33683	0.775149	0.00197428
0.976183	2.37942	0.768243	0.00215639
0.974977	2.42278	0.761156	0.00235492
0.973712	2.46693	0.753885	0.00257131
0.972385	2.51189	0.746427	0.0028071
0.970994	2.55766	0.73878	0.00306398
0.969536	2.60427	0.730943	0.00334371
0.968007	2.65173	0.722914	0.00364826
0.966405	2.70005	0.714691	0.00397974
0.964726	2.74926	0.706274	0.00434039
0.962967	2.79936	0.697661	0.00473264
0.961126	2.85037	0.688853	0.00515913
0.959197	2.90232	0.679848	0.00562264
0.957179	2.95521	0.670646	0.00612621
0.955066	3.00906	0.66125	0.00667307
0.952856	3.0639	0.651658	0.0072667
0.950544	3.11973	0.641874	0.00791076
0.948127	3.17659	0.631899	0.00860925
0.9456	3.23448	0.621735	0.00936638
0.942959	3.29342	0.611385	0.0101866
0.940201	3.35344	0.600852	0.0110749

0.93732	3.41455	0.590141	0.0120361
0.934313	3.47677	0.579257	0.0130757
0.931175	3.54013	0.568204	0.0141995
0.927902	3.60465	0.556989	0.0154135
0.924488	3.67034	0.545618	0.016724
0.920931	3.73722	0.534098	0.0181378
0.917225	3.80533	0.522437	0.0196618
0.913366	3.87468	0.510645	0.0213035
0.90935	3.94529	0.49873	0.0230707
0.905172	4.01718	0.486702	0.0249713
0.900827	4.09039	0.474573	0.0270138
0.896313	4.16493	0.462353	0.0292069
0.891623	4.24083	0.450055	0.0315595
0.886756	4.31811	0.437691	0.0340809
0.881707	4.39681	0.425276	0.0367806
0.876472	4.47693	0.412823	0.0396685
0.871047	4.55852	0.400346	0.0427545
0.865431	4.64159	0.387862	0.0460486
0.859619	4.72617	0.375385	0.0495611
0.85361	4.8123	0.362931	0.0533023
0.847401	4.9	0.350517	0.0572824
0.84099	4.9893	0.33816	0.0615117
0.834375	5.08022	0.325876	0.0660002
0.827556	5.1728	0.313683	0.0707578
0.820531	5.26706	0.301597	0.0757943
0.813301	5.36305	0.289636	0.0811188
0.805866	5.46078	0.277816	0.0867402
0.798226	5.5603	0.266154	0.0926668
0.790382	5.66163	0.254665	0.0989064
0.782338	5.7648	0.243367	0.105466
0.774094	5.86986	0.232273	0.112352
0.765654	5.97683	0.221399	0.119569
0.757021	6.08574	0.210758	0.127122
0.7482	6.19665	0.200364	0.135014
0.739195	6.30957	0.190228	0.143248
0.730012	6.42456	0.180362	0.151824
0.720656	6.54163	0.170776	0.160742
0.711135	6.66085	0.161478	0.170001
0.701454	6.78223	0.152477	0.179598
0.691621	6.90583	0.143778	0.189527
0.681646	7.03168	0.135389	0.199784
0.671535	7.15982	0.127312	0.210362
0.661298	7.2903	0.119551	0.221251
0.650946	7.42315	0.112107	0.232441
0.640487	7.55843	0.104981	0.243922
0.629931	7.69617	0.0981714	0.25568
0.61929	7.83642	0.0916774	0.267701
0.608573	7.97923	0.0854956	0.279971

0.597793	8.12464	0.0796219	0.292472
0.586959	8.2727	0.0740515	0.305187
0.576084	8.42345	0.0687784	0.318098
0.565179	8.57696	0.0637958	0.331187
0.554254	8.73326	0.0590965	0.344432
0.543321	8.89241	0.0546722	0.357814
0.532392	9.05446	0.0505143	0.371311
0.521477	9.21947	0.0466136	0.384903
0.510587	9.38748	0.0429606	0.398569
0.499733	9.55855	0.0395454	0.412286
0.488925	9.73274	0.036358	0.426035
0.478173	9.91011	0.033388	0.439793
0.467487	10.0907	0.0306251	0.453539
0.456877	10.2746	0.028059	0.467255
0.446351	10.4618	0.0256794	0.480919
0.435917	10.6525	0.0234761	0.494514
0.425585	10.8466	0.0214392	0.508019
0.415361	11.0443	0.0195588	0.521419
0.405253	11.2455	0.0178254	0.534695
0.395268	11.4505	0.0162297	0.547833
0.385412	11.6591	0.0147627	0.560817
0.37569	11.8716	0.0134159	0.573634
0.366108	12.088	0.012181	0.58627
0.356671	12.3082	0.0110501	0.598714
0.347383	12.5325	0.0100158	0.610955
0.338248	12.7609	0.0090708	0.622984
0.329269	12.9935	0.00820846	0.634791
0.320449	13.2303	0.00742241	0.64637
0.311791	13.4714	0.00670665	0.657713
0.303298	13.7169	0.00605558	0.668814
0.294969	13.9668	0.00546393	0.679669
0.286808	14.2214	0.0049268	0.690275
0.278815	14.4805	0.00443961	0.700628
0.27099	14.7444	0.00399813	0.710725
0.263334	15.0131	0.0035984	0.720566
0.255847	15.2867	0.00323677	0.73015
0.248528	15.5653	0.00290989	0.739476
0.241377	15.8489	0.00261462	0.748546
0.234393	16.1378	0.00234812	0.75736
0.227576	16.4318	0.00210775	0.765921
0.220922	16.7313	0.0018911	0.774231
0.214432	17.0362	0.00169596	0.782292
0.208104	17.3467	0.00152029	0.790107
0.201934	17.6628	0.00136225	0.79768
0.195923	17.9846	0.00122016	0.805015
0.190067	18.3124	0.00109247	0.812116
0.184364	18.6461	0.000977793	0.818987
0.178812	18.9859	0.000874846	0.825633

0.173408	19.3319	0.000782477	0.832058
0.16815	19.6842	0.000699636	0.838267
0.163035	20.0429	0.000625376	0.844266
0.158061	20.4082	0.000558834	0.850059
0.153225	20.7801	0.000499233	0.855652
0.148524	21.1588	0.00044587	0.861049
0.143955	21.5443	0.00039811	0.866257
0.139515	21.937	0.000355379	0.87128
0.135203	22.3367	0.000317162	0.876123
0.131014	22.7438	0.000282991	0.880792
0.126946	23.1583	0.000252449	0.885293
0.122996	23.5803	0.000225157	0.889629
0.119162	24.01	0.000200777	0.893807
0.11544	24.4475	0.000179005	0.897831
0.111828	24.8931	0.000159565	0.901706
0.108323	25.3467	0.000142213	0.905437
0.104923	25.8086	0.000126727	0.909029
0.101624	26.2789	0.000112911	0.912486
0.0984246	26.7578	0.000100587	0.915814
0.0953214	27.2455	8.9595e-05	0.919016
0.0923121	27.742	7.9794e-05	0.922097
0.0893942	28.2475	7.10563e-05	0.925062
0.0865651	28.7623	6.32679e-05	0.927913
0.0838224	29.2864	5.63267e-05	0.930656
0.0811638	29.8201	5.01417e-05	0.933295
0.0785868	30.3636	4.46312e-05	0.935832
0.0760892	30.9169	3.97224e-05	0.938272
0.0736688	31.4803	3.53503e-05	0.940618
0.0713232	32.054	3.14565e-05	0.942875
0.0690505	32.6381	2.79893e-05	0.945044
0.0668484	33.2329	2.49023e-05	0.94713
0.0647149	33.8386	2.2154e-05	0.949136
0.062648	34.4552	1.97076e-05	0.951064
0.0606457	35.0831	1.75302e-05	0.952917
0.0587062	35.7224	1.55923e-05	0.954699
0.0568275	36.3734	1.38677e-05	0.956413
0.0550079	37.0363	1.23332e-05	0.95806
0.0532456	37.7112	1.09678e-05	0.959643
0.0515387	38.3985	9.75309e-06	0.961165
0.0498858	39.0982	8.67245e-06	0.962628
0.0482851	39.8107	7.71116e-06	0.964035
0.0467351	40.5362	6.85611e-06	0.965387
0.0452341	41.2749	6.09561e-06	0.966687
0.0437808	42.0271	5.41923e-06	0.967937
0.0423736	42.793	4.81771e-06	0.969138
0.0410111	43.5728	4.2828e-06	0.970294
0.039692	44.3669	3.80714e-06	0.971404
0.0384148	45.1754	3.38419e-06	0.972472

0.0371784	45.9986	3.00813e-06	0.973499
0.0359814	46.8369	2.67377e-06	0.974486
0.0348226	47.6904	2.37651e-06	0.975435
0.0337008	48.5595	2.11224e-06	0.976348
0.0326148	49.4445	1.87731e-06	0.977225
0.0315636	50.3455	1.66846e-06	0.978069
0.030546	51.263	1.48281e-06	0.978881
0.029561	52.1972	1.31779e-06	0.979662
0.0286076	53.1484	1.17111e-06	0.980412
0.0276847	54.117	1.04073e-06	0.981134
0.0267914	55.1032	9.24852e-07	0.981829
0.0259268	56.1073	8.21859e-07	0.982497
0.0250899	57.1298	7.30322e-07	0.98314
0.0242799	58.1709	6.4897e-07	0.983758
0.023496	59.231	5.7667e-07	0.984353
0.0227372	60.3104	5.12417e-07	0.984925
0.0220029	61.4095	4.55316e-07	0.985475
0.0212921	62.5286	4.04573e-07	0.986005
0.0206043	63.6681	3.5948e-07	0.986514
0.0199385	64.8283	3.1941e-07	0.987005
0.0192942	66.0097	2.83802e-07	0.987477
0.0186707	67.2126	2.52161e-07	0.987931
0.0180672	68.4375	2.24046e-07	0.988368
0.0174832	69.6847	1.99063e-07	0.988789
0.016918	70.9546	1.76864e-07	0.989194
0.0163711	72.2476	1.57139e-07	0.989584
0.0158417	73.5642	1.39613e-07	0.989959
0.0153295	74.9048	1.24041e-07	0.99032
0.0148338	76.2699	1.10204e-07	0.990668
0.014354	77.6598	9.79106e-08	0.991003
0.0138898	79.075	8.69877e-08	0.991325
0.0134405	80.516	7.72828e-08	0.991636
0.0130057	81.9833	6.86603e-08	0.991935
0.012585	83.4773	6.09993e-08	0.992223
0.0121779	84.9986	5.41929e-08	0.9925
0.0117839	86.5476	4.81456e-08	0.992767
0.0114026	88.1248	4.2773e-08	0.993024
0.0110337	89.7307	3.79997e-08	0.993272
0.0106767	91.3659	3.37589e-08	0.993511
0.0103312	93.031	2.99912e-08	0.99374
0.00999686	94.7263	2.66439e-08	0.993962
0.00967334	96.4526	2.36702e-08	0.994175
0.00936029	98.2103	2.10282e-08	0.994381
0.00905735	100	1.8681e-08	0.994579