SD92-15-F

SD Department of Transportation
Office of Research

Freezing Properties of Deicing Mixtures

Study SD92-15
Final Report

Prepared by
SD Department of Transportation
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16. Abstract

This report formalizes the information provided to the contract monitor during the period of the contract. The contract involved the performance of measurements on specimens identified by label only (blind study).

Cooling curves have been determined for nine complex salts for approximately 50% saturated solutions, and for two of the salts (DOT4 #13 and DOT4 #15) at a number of concentrations, expressed as salt/water ratio by weight, from 0.05 up to approximately 0.57. From these curves, the portion of the phase diagram for the solution/pure ice region was constructed. The results indicate the quality of the data and the efficacy of the method for determining this portion of the phase diagram.

Measurements have been made of the shear strength of ice frozen onto concrete substrates whose surfaces were treated with different concentrations of the salt solutions for two salts. The results indicate that one of the samples (DOT4 #13) does mitigate adhesive strength better that sodium chloride, but not as well as the original batch of South Dakota Deicer #2 tested in 1988.

A device was constructed in accordance with Midwest Research Institute specifications for the measurement of salt penetration of ice. The results did not show any strong penetration properties, but the test really needed larger crystals or pellets of the salts to provide conclusive evidence.

In accordance with the contract, this report includes only the data obtained and the construction of the phase curves for two salts; no further analysis nor the formulation of any conclusions or recommendations is presented.

17. Keyword	18. Distribution Statement
Deicing Mixtures, Cooling Curves, Phase Diagram, Shear Strength, Penetration.	No restrictions. This document is available to the public from the sponsoring agency.

19. Security Classification (of this report)	Security Classification (of this page)	21. No. of Pages	22. Price
Unclassified	Unclassified		

DISCLAIMER

EXECUTIVE SUMMARY

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Cooling curves have been determined for nine complex salts for approximately 50% saturated solutions, and for two of the salts (DOT4 #13 and DOT4 #15) at a number of concentrations, expressed as salt/water ration by weight, from 0.00 up to approximately 0.57. From these curves, the phase curve for the solution/pure ice region was constructed. The results indicates the quality of the data and the efficacy of the method for determining this portion of the phase diagram.

Measurements have been made of the shear strength of ice frozen onto concrete substrates treated with different concentrations of the salt solutions for two salts. The results indicate that one of the samples (DOT4 #13) does mitigate adhesive strength better that sodium chloride, but not as well as the original batch of South Dakota Deicer #2 tested in 1988.

A device was constructed in accordance with Midwest Research Institute specifications for the measurement of salt penetration of ice. The results did not show any strong penetration properties, but the test really needed larger crystals or pellets of the salts to provide conclusive evidence.

This report does not include any analysis of the data obtained beyond the construction of the phase curves, nor the formulation of any conclusions or recommendations, since the contract was for the obtaining of data only.

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I. STATEMENT OF PROBLEM

Mr. Daniel P. Johnston developed a series of salts as part of his study of materials for the mitigation of highway icing. In order to further characterize these salts, which were identified only by an alphanumeric label, further information was needed on the freezing characteristics of the materials, and their ability of the materials to penetrated ice. Determination of these properties was specified in South Dakota Department of Transportation Agreement #310167, Study SD92-15.

II. RESEARCH OBJECTIVES

In accordance with Agreement #310167, the objectives of this research were:

1. to obtain freezing point data of 50% saturated solutions for a series of 10 chemical mixtures supplied by the State;
2. to construct a partial phase diagram (i.e. equilibrium line between solution and pure ice) for two of these mixtures using fixed concentrations of the material over the solubility range;
3. to measure the ice penetration properties of three of these materials using appropriate procedures and compare against a control sample of sodium chloride;
4. to perform any required ancillary work as appropriate in order to accomplish the above tasks.

In June, 1993, Mr. Johnston requested that we revise the scope of the work to be performed to also include some shear strength measurements in the study; he indicated that he needed this information for the submission of a patent application, and that he wanted these measurements to be performed immediately. We agreed to attempt this, with the condition that we probably would have to modify or eliminate some of the objectives listed above since the work was to be performed under the budget stipulated in Agreement #310167. Also, in order to accommodate this request, we would have to significantly delay other work which would have to be caught up later. All of the data specified under the modified objectives of the contract were obtained and delivered to Mr. Johnston during the period of the contract. Preparation of this formal report of Study SD92-15 was left until this time in order that other commitments which had been delayed could be completed.

Because the objectives of this research were simply to obtain the data and the construction of the partial phase diagram (the phase curve for the solution/pure ice region) for two salts, as specified in Agreement #310167 as modified by mutual consent, no further analysis of the data has been performed under the contract.

III. METHODS OF MEASUREMENT

The properties of the salts were determined using the equipment and methods which are summarized as follows:

a. For the measurement of cooling-curves, from which the freezing point data for 50% saturated solutions of the salts were determined, an improved apparatus has been developed. It is based on the system described in the final report for South Dakota Department of Transportation Contract #3213 entitled "A Study of South Dakota Deicer Number 2: Final Report, dated September, 1988 (hereinafter referred to as SDDOT1).

Since the identity of the salts was unknown to us, we used estimates of the salt/water ratio (by weight) for salts used in previous research (see SDDOT1, p23) to make approximately 50% saturated solutions for each sample. All data in this current report is given in terms of the salt/water ratio. Cooling curves obtained for several solutions of up to approximately 0.56 salt/water ratio were used to construct the phase diagrams for two salts.

The cooling curve apparatus is described in more detail in Section IV.

b. For the measurement of the shear strength of ice on concrete surfaces treated with various concentrations of the salts, the apparatus and measurement protocol developed under South Dakota Department of Transportation Contract #3213 was used. This is described in SDDOT1.

c. For the measurement of the penetration of a salt crystal or pellet into ice to determine the penetration capabilities of the salts provided, a device was fabricated in accordance with the design developed by the Midwest Research Institute (MRI) under the direction of Mr. Robert R. Blackburn.

IV. COOLING-CURVES AND PHASE DIAGRAMS

The cooling-curve apparatus used in this work is based on the device described in SDDOT1. Several improvements have been incorporated in order to develop the instrument towards having the capability of the determination of quantitative thermodynamic parameters. An improved vacuum capability, significant reduction of radiative heat transfers, a much more constant heat sink, and a heat-flux meter have been incorporated. This work has been performed by Ashworth & Associates, to whom the instrument belongs. There is still work to be done on the stabilization of the calibration of the heat-flux meter, but the quality and range of the cooling curves obtained has been much improved over the system described in SDDOT1.

Figure 1 shows a schematic representation of the apparatus. The main components are a bell jar which can be evacuated to a pressure of 10^{-6} Torr, an integrated liquid nitrogen container, and the specimen cell assembly. Energy is removed from the sample cell via a heat-flux meter which comprises a nylon post incorporating a multiple element thermocouple; the thermocouple wires are responsible for the major part of the heat flow; energy is dissipated into the liquid nitrogen bath via a copper coupling. In this manner, the temperature of the heat sink remains almost constant during the course of the experiment. A stirrer, which includes the thermocouple used to measure the specimen temperature, is driven in a steady reciprocating action by a mechanism which prevents damage to itself when the specimen becomes solid.

Specimens are loaded in the form of solutions. They are removed by placing a small tube into the specimen cell (after the stirrer has been removed) and pressurizing the cell with nitrogen gas. Several cycles of filling, brushing, and fluid removal (starting with warm tap water and ending with rinses with distilled water) followed by drying with warm gas are used to cleanse the cell before the next specimen is loaded.

The quality of the cooling curves can be determined by inspection of the data provided. Figure 2 shows the cooling curve for pure water. The flatness of the curve during the removal of latent heat shows the clarity with which a first order phase transition is revealed. The relative slopes of the curve above and below 0°C indicate the ability to distinguish changes in specific heats, the extent of the curve indicates the significantly improved ability to reach lower temperatures (below -70 °C), the smoothness of the curve between 0°C and -70°C indicates the thermal stability of the system. And the final portion of the curve demonstrates the added ability to investigate the specimen in both cooling and heating modes; apart from the fact that heating was carried out more quickly than the cooling, the consistency of the information obtained in the two modes can be seen.

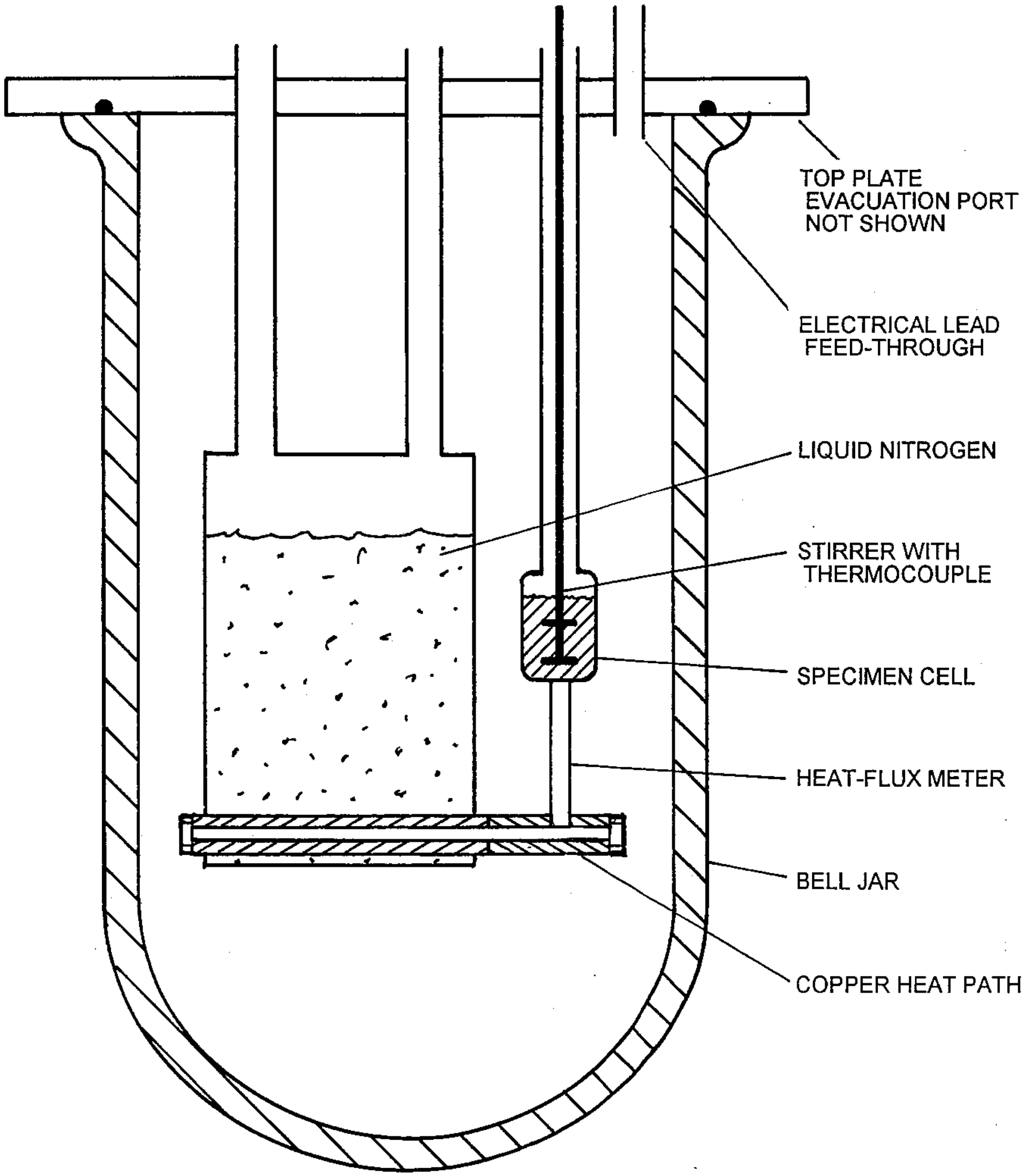


FIGURE 1. COOLING CURVE APPARATUS

Figure 3 shows the cooling curve for sodium chloride solution. The features of the phase diagram of a binary system are clearly indicated. As heat is removed, the temperature of the solution is lowered until the phase region boundary is encountered at about -7°C, the ensuing "slide" down the phase curve as pure H_2O is removed and the concentration of the solution increases until the eutectic point is reached at about -23°C. After latent heat is removed as the solution solidifies, further cooling occurs at a rate determined by the specific heat of the solid. On heating, the same features are seen in reverse with the exception that there is no equivalent of the supercooling seen on cooling; this indicates that the supercooling is a metastable state. The small difference indicated in the eutectic temperature for cooling and heating are due to imperfect thermal equilibrium within the cell when the specimen is solid.

Figures 4 through 23 show the cooling curves for 20 solutions of the salts provided. All of these solutions are made from Batch #1 salts (supplied by Mr. Johnston on 12 November, 1992); salt provided for the previous rough measurements were designated as Batch #0 (supplied by Mr. Johnston in July, 1992). The specimen designation is formulated as DOT4 #BNX where B is the Batch number, N is the salt sample Number indicated by DOT personnel, and the X distinguishes each individual specimen made from a given salt sample; e.g., specimen DOT4 #15D was the fourth specimen made from sample 5 of Batch #1; for samples 3 and 5, specimens with different concentrations were made and measured in order to construct the phase diagrams.

Tables I and II give the data interpolated from the cooling-curves for samples 3 and 5; Figures 24 and 25 show the phase diagrams which were constructed from these data. Although no difficulty was expected in the construction of these phase diagrams, the quality of the data obtained, as measured by the R squared factor for the quadratic curves fitted, was even better than expected. R squared values of better than 0.999, with at least four degrees of freedom, were obtained for both samples. We feel that the efficacy of the method used for the determination of these portions of the phase diagram has been confirmed.

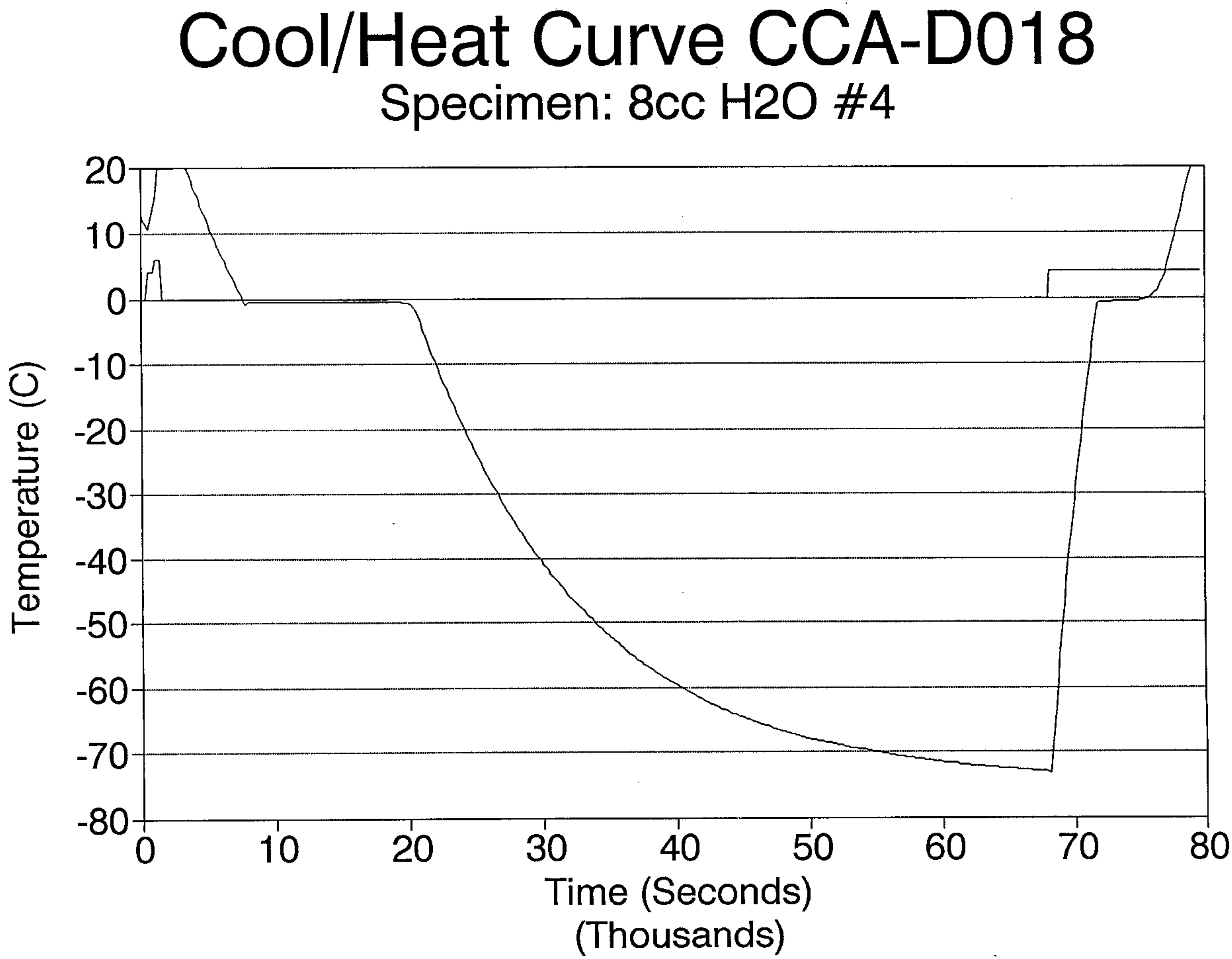
V. SHEAR STRENGTH MEASUREMENT

These measurements were undertaken to determine the ability of the salts to weaken the bond strength of ice frozen to treated surfaces. As indicated in Section III, the apparatus and measurement protocol developed under South Dakota Department of Transportation Contract #3213 was used. These are described in some detail in Section II of SDDOT1. In order to speed-up the data acquisition, the full protocol for specimen cleaning between specimens was relaxed when one treatment of a given material followed one with the same material at a lower treatment rate.

Data was obtained for samples DOT4 #13 and DOT4 #17 per Mr. Johnston's instructions. These are shown in Tables III and IV, and in Figures 26 and 27; the effectiveness of DOT4 #17 is similar to that of NaCl. Clearly, DOT4 #13 causes considerably more bond strength mitigation than DOT4 #17 and NaCl, but it is not as good as the original sample of SD Deicer #2.

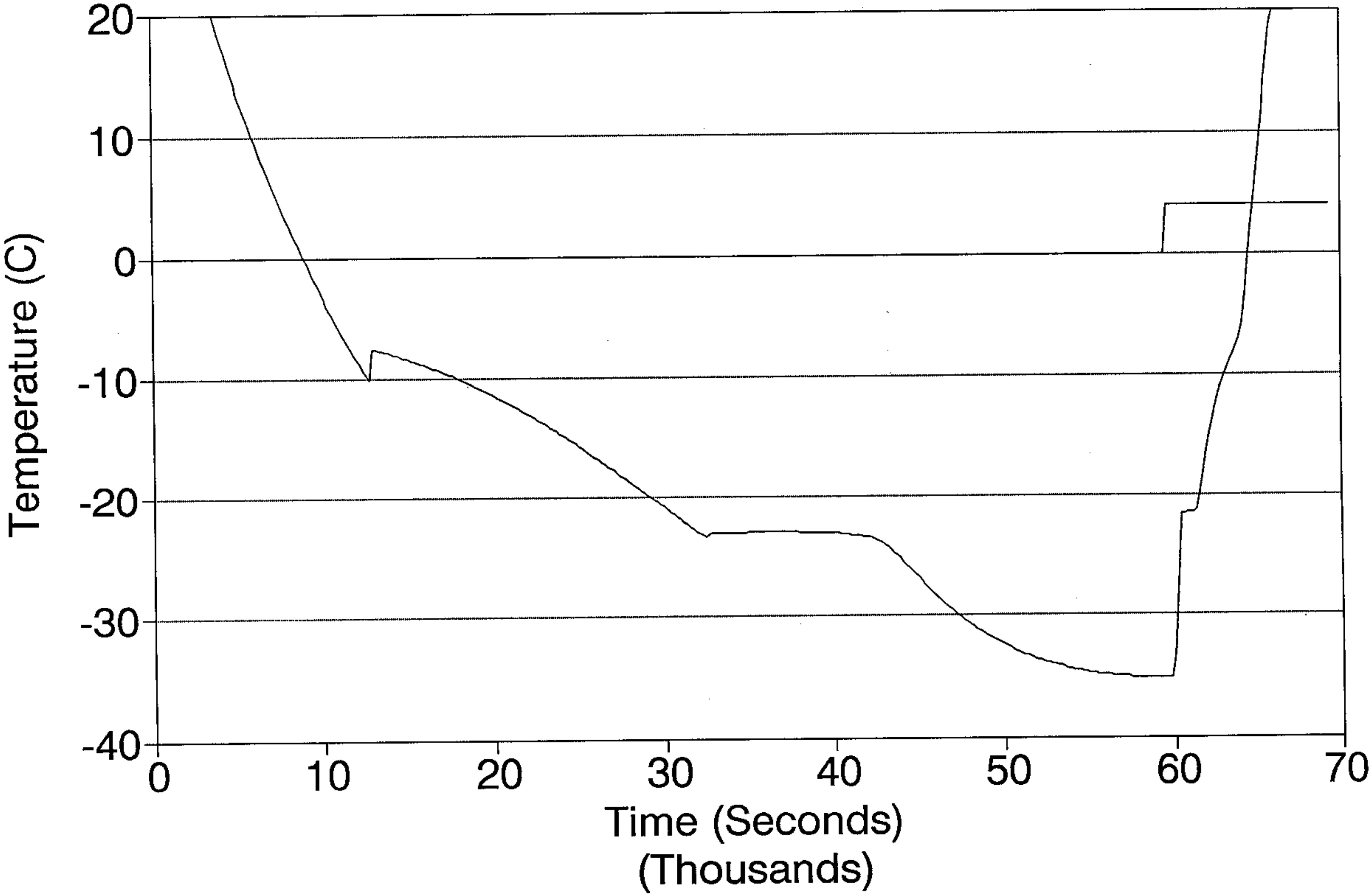
VI. PENETRATION DEPTH MEASUREMENT

A device was fabricated for salt penetration measurements following the design developed by MRI. It consists of a vertical Plexiglas plate with 10 countersunk holes of diameter 0.156", and a base plate which keeps the holes vertical. Graph paper (centimeter and millimeter gradations) was attached behind the vertical plate to give a reference scale against which to measure. The procedure for a penetration measurement is to freeze water in the holes in a manner which produces clear, bubble-free, untracked ice in the holes. Each ice column was adjusted to the same height of 1mm below the top of the plate, and the assembly allowed to equilibrate at the temperature at the required temperature. Measured quantities of the salt and a red food dye were then placed on the top of the ice columns. The system was then photographed periodically to record the amount of penetration.


Cool/Heat Curve CCA-D018
Specimen: 8cc H2O #4
Temperature (C)
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
0
10
20
30
40
50
60
70
80
Time (Seconds)
(Thousands)

Cool/Heat Curve CCA-D013

Specimen: 2cc NaCl + 4cc Dist. H2O



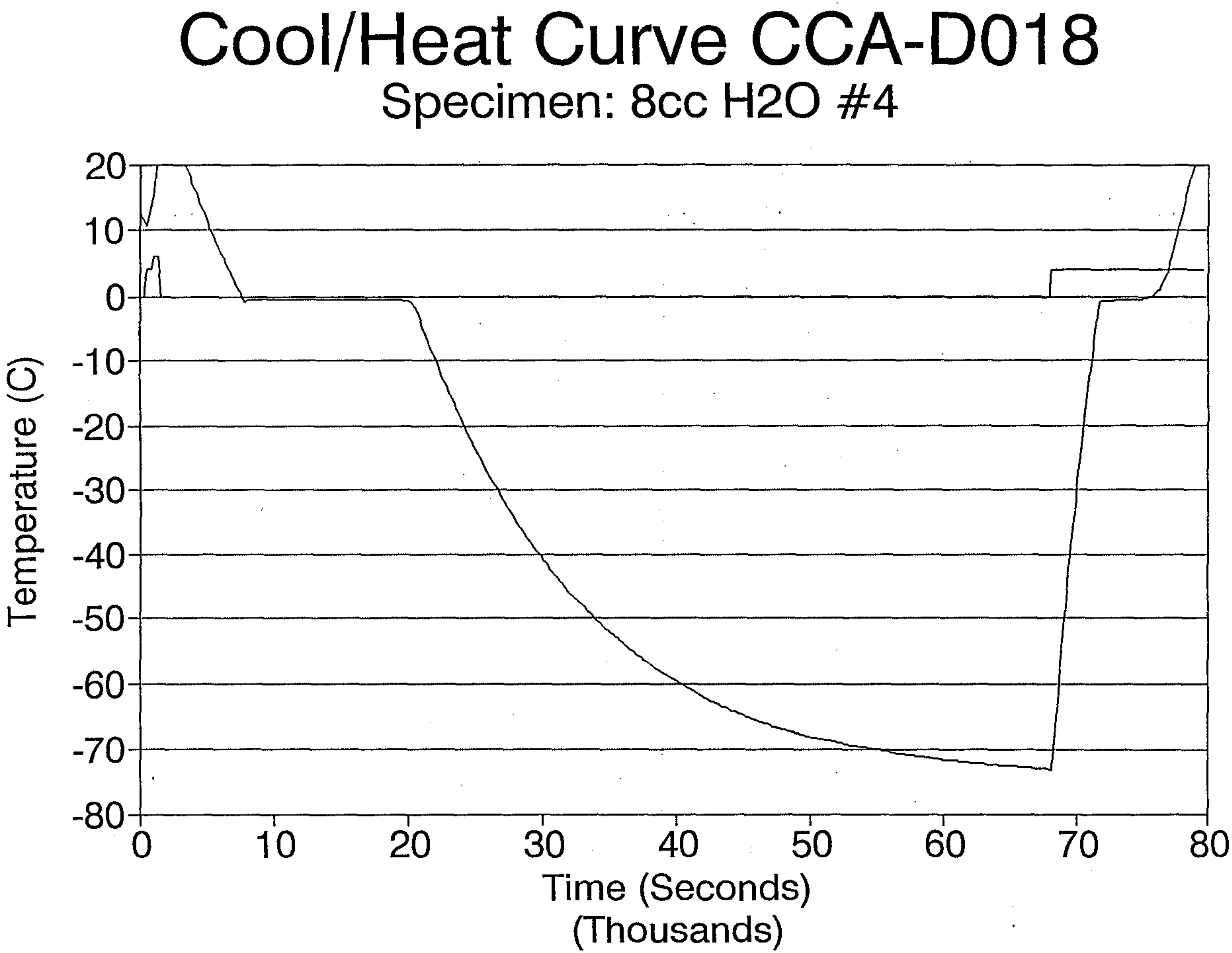


Figure 2: CCA-D018: Cool/Heat Curve for Distilled Water.

TABLE I.
Data and Regression Analysis for Specimen DOT4 #13

File CCA-A001.WQ1

Analysis and Construction of Phase Diagram
Specimen: SDOT4, Batch 1, Sample DOT4 #13.

File	S/H2O	T(Deg C) Measured	T(Deg C) Calculated	X	X^2
	0	0	-0.14264	0	0
CCA-D034	0.05203	-2.45	-2.08696	0.05203	0.002707
CCA-D035	0.14963	-5.58	-5.85829	0.14963	0.022389
CCA-D019	0.27967	-11.15	-11.1347	0.27967	0.078215
CCA-D036	0.34948	-13.95	-14.0858	0.34948	0.122136
CCA-D033	0.47346	-19.90	-19.5311	0.47346	0.224164
CCA-D037	0.57082	-23.80	-23.9904	0.57082	0.325835

Regression Output:

Constant		-0.14264
Std Err of Y Est		0.324266
R Squared		0.999115
No. of Observations		7
Degrees of Freedom		4
X Coefficient(s)	-36.9269	-8.49857
Std Err of Coef.	2.254459	3.883498

TABLE II.
Data and Regression Analysis for Specimen DOT4 #15

File CCA-A002.WQ1

Analysis and Construction of Phase Diagram
Specimen: DOT4, Batch 1, Sample DOT4 #15.

File	S/H2O	T(Deg C) Measured	T(Deg C) Calculated	X	X^2
	0.00000	0	-0.133	0	0
CCA-D028	0.05285	-2.19	-1.982	0.05285	0.002793
CCA-D029	0.10007	-3.88	-3.671	0.10007	0.010014
CCA-D030	0.14864	-5.16	-5.446	0.14864	0.022094
CCA-D021	0.25843	-9.48	-9.596	0.25843	0.066786
CCA-D031	0.35449	-13.40	-13.385	0.35449	0.125663
CCA-D032	0.45827	-17.87	-17.645	0.45827	0.210011
CCA-D039	0.55668	-21.72	-21.842	0.55668	0.309893

Regression Output:

Constant		-0.13314
Std Err of Y Est		0.23061
R Squared		0.999379
No. of Observations		8
Degrees of Freedom		5
X Coefficient(s)	-34.5567	-7.97608
Std Err of Coef.	1.663105	2.924237

TABLE III.
Shear Strength of Ice on Concrete treated with DOT4 #17.

DATA FILE NAME: A&A01D93
TEST SERIES: A2 18JUL93-13OCT93
TREATMENT: DOT4 #17 (Batch 1 No. 7)
SUBSTRATE: Standard Highway Concrete
TEST CONSTANT: TEMP = -10 C
CALIBRATION: based on 04JAN88 data and sample area of 12.07 cm2
0.0387 * GAUGE - 0.15029 = TRUE Kg/cm2

APPL RATE (lb/LM)	SHEAR STRENGT (KG/CM2)	STAND DEV (KG/CM2)	CONVERTED DATA 1	2	3	4	5	6	7	8	RAW DATA 1	2	3	4	5	6	7	8
0	7.83	0.81	6.43	8.56	6.82	7.98	7.78	7.98	7.98	9.14	170	225	180	210	205	210	210	240
1	8.12	0.58	8.56	7.40		8.75	7.59	7.40	8.36	8.75	225	195	80	230	200	195	220	230
3	7.69	0.29	7.40	7.59	7.59	7.40	7.78	7.59	7.78	8.36	195	200	200	195	205	200	205	220
10	7.18	0.92	6.82	8.17		6.82	8.94	6.43	6.24	6.82	180	215	110	180	235	170	165	180
25	7.06	0.62	5.77	6.85	7.20	7.82	7.74	7.44	6.70	6.97	153	181	190	206	204	196	177	184
50	6.96	0.88	6.82	7.74	7.94	6.97	6.27	6.12	5.62	8.21	180	204	209	184	166	162	149	216
100	5.62	0.93	5.00	4.73	6.39	6.58	5.62	3.87	6.20	6.54	133	126	169	174	149	104	164	173
150	4.82	1.47	3.49	2.79	5.85	5.73	5.50	3.33	4.46	7.40	94	76	155	152	146	90	119	195
200	5.62	0.93	5.00	4.73	6.39	6.58	5.62	3.87	6.20	6.54	133	126	169	174	149	104	164	173
250	5.62	0.93	5.00	4.73	6.39	6.58	5.62	3.87	6.20	6.54	133	126	169	174	149	104	164	173
300	5.62	0.93	5.00	4.73	6.39	6.58	5.62	3.87	6.20	6.54	133	126	169	174	149	104	164	173
400	5.62	0.93	5.00	4.73	6.39	6.58	5.62	3.87	6.20	6.54	133	126	169	174	149	104	164	173

TABLE IV.

Shear Strength of Ice on Concrete treated with DOT4 #13.

DATA FILE NAME: A&A02D93
TEST SERIES: A2 12AUG93-20SEP93
TREATMENT: DOT4 #13 (Batch 1 No. 3)
SUBSTRATE: Standard Highway Concrete
TEST CONSTANT: TEMP = -10 C
CALIBRATION: based on 04JAN88 data and sample area of 12.07 cm2
0.0387 * GAUGE - 0.15029 = TRUE Kg/cm2

APPL RATE (lb/LM)	SHEAR STRENGT (KG/CM2)	STAND DEV (KG/CM2)	CONVERTED DATA 1	2	3	4	5	6	7	8	RAW DATA 1	2	3	4	5	6	7	8
0	7.54	0.74	6.58	8.33	7.05	8.60	6.78	8.33	7.63	7.01	174	219	186	226	179	219	201	185
0	6.85	0.47	6.66	6.66	6.70	7.78	7.16	7.16	6.12	6.58	176	176	177	205	189	189	162	174
1	6.58	0.98	6.62	7.47	4.76	7.59	5.23	7.28	7.05	6.66	175	197	127	200	139	192	186	176
3	6.87	0.55	7.28	6.97	7.63	7.44	6.54	6.93	6.20	6.00	192	184	201	196	173	183	164	159
10	6.81	1.15	6.39	7.71	6.58	9.22	5.04	6.85	6.00	6.66	169	203	174	242	134	181	159	176
25	7.09	0.57	6.82	6.97	7.44	8.40	6.85	7.16	6.43	6.66	180	184	196	221	181	189	170	176
50	5.27	2.11	8.60	8.56	2.91	6.24	3.49	4.46	4.22	3.72	226	225	79	165	94	119	113	100
100	4.96	0.74	5.42	5.23	5.42	6.39	4.26	4.57	4.03	4.34	144	139	144	169	114	122	108	116
150	4.26	0.77	4.26	4.69	5.00	5.65	3.72	3.72	3.10	3.95	114	125	133	150	100	100	84	106
200	3.25	0.67	4.26	3.57	3.72	3.87	2.98	2.71	2.17	2.71	114	96	100	104	81	74	60	74
250	2.25	0.73	3.33	2.83	2.52	2.60	2.48	1.20	1.13	1.90	90	77	69	71	68	35	33	53
300	1.39	0.52	2.44	1.82	1.28	0.97	1.55	1.05	0.66	1.36	67	51	37	29	44	31	21	39

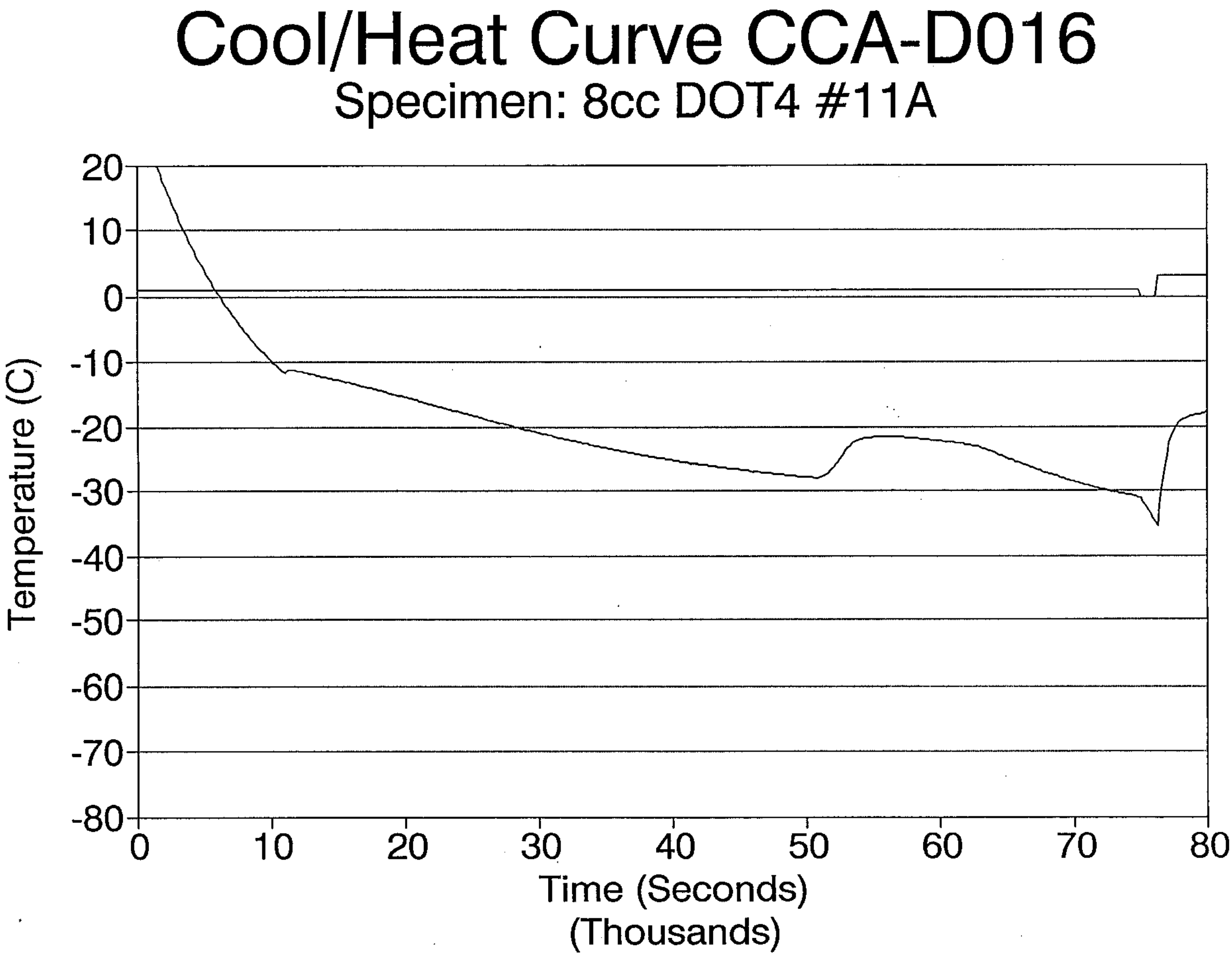


Figure 4: CCA-D016: Cool/Heat Curve for DOT4 #11A.

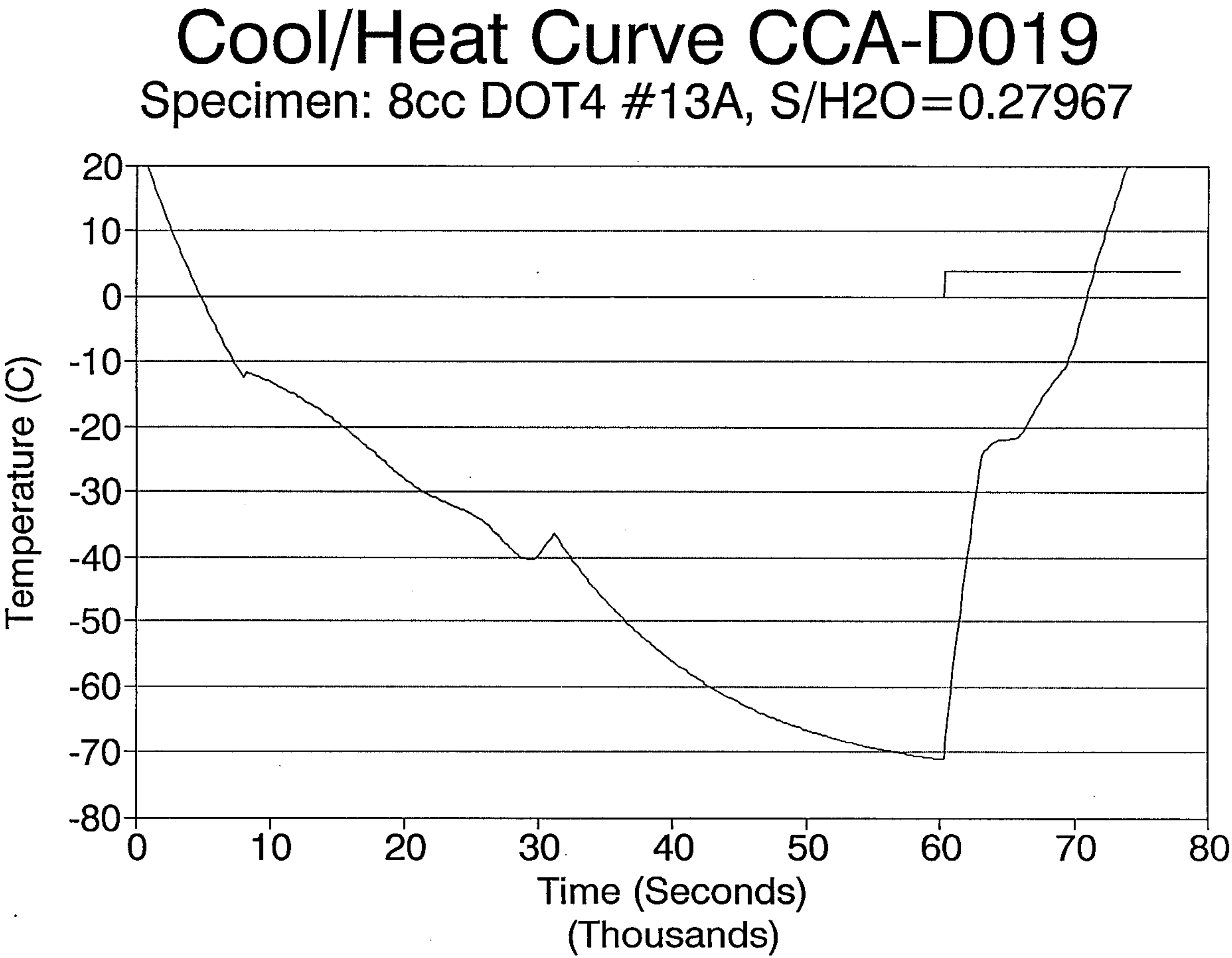


Figure 5: CCA-D019: Cool/Heat Curve for DOT4 #13A.

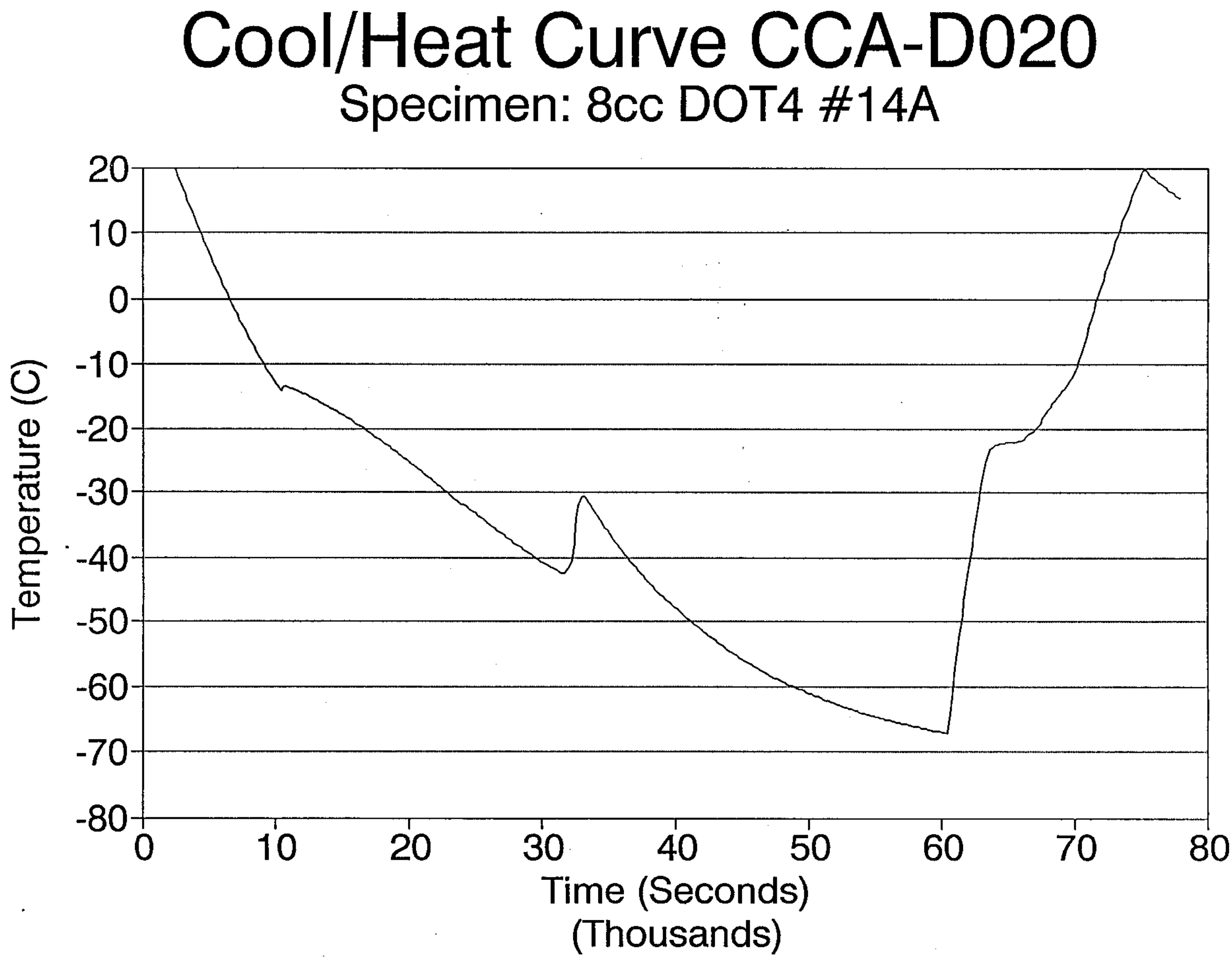


Figure 6: CCA-D020: Cool/Heat Curve for DOT4 #14A.

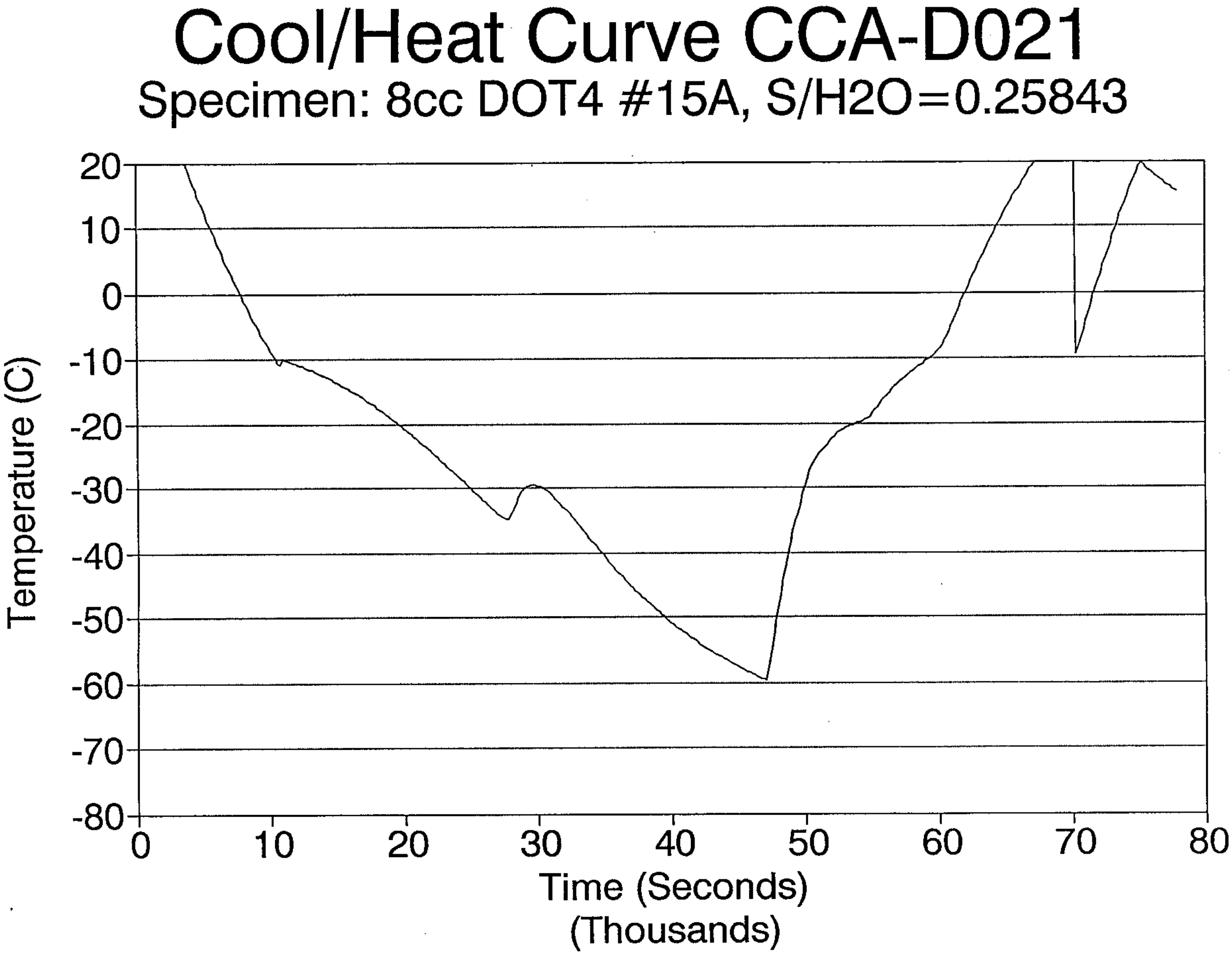


Figure 7: CCA-D021: Cool/Heat Curve for DOT4 #15A.

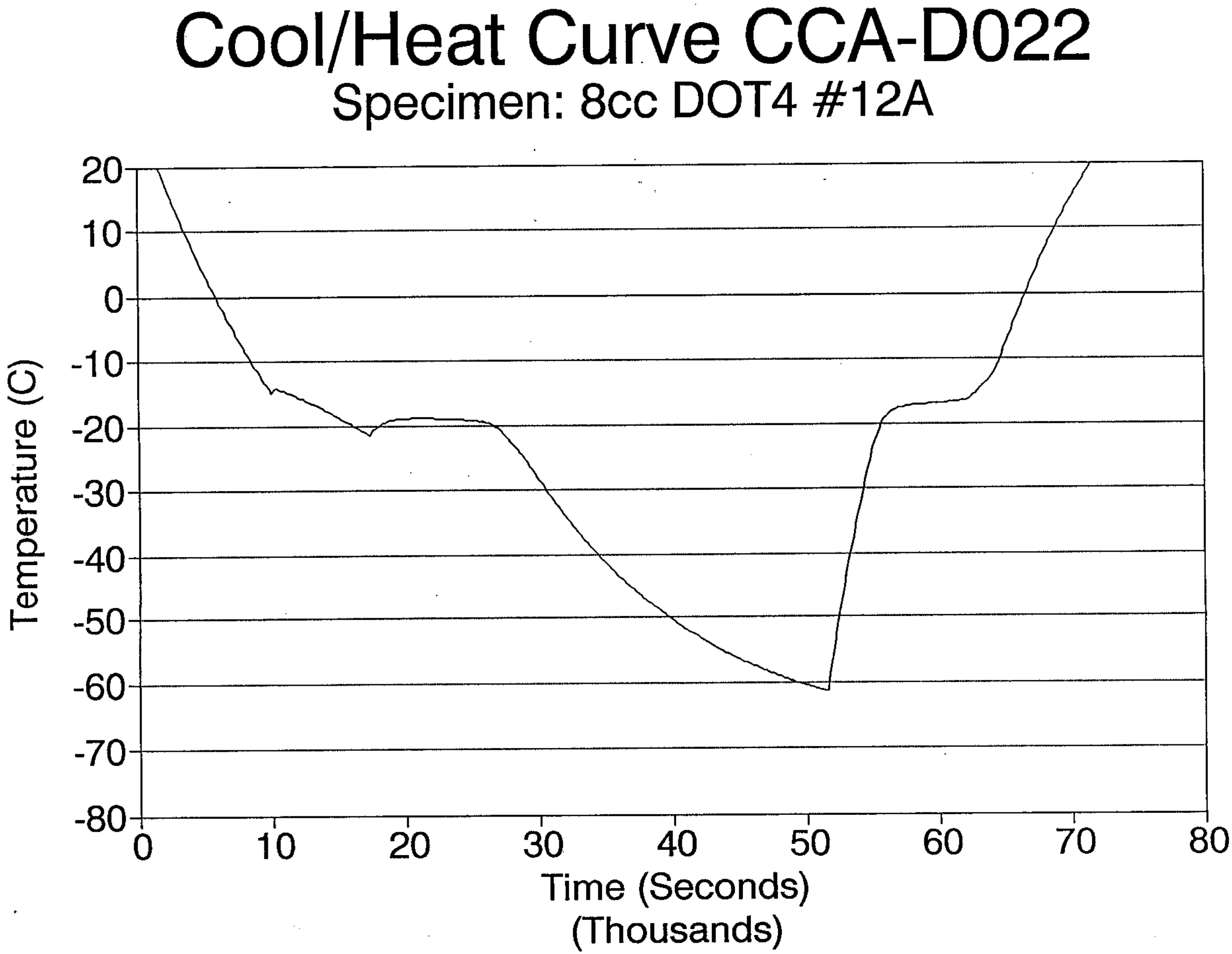


Figure 8: CCA-D022: Cool/Heat Curve for DOT4 #12A.

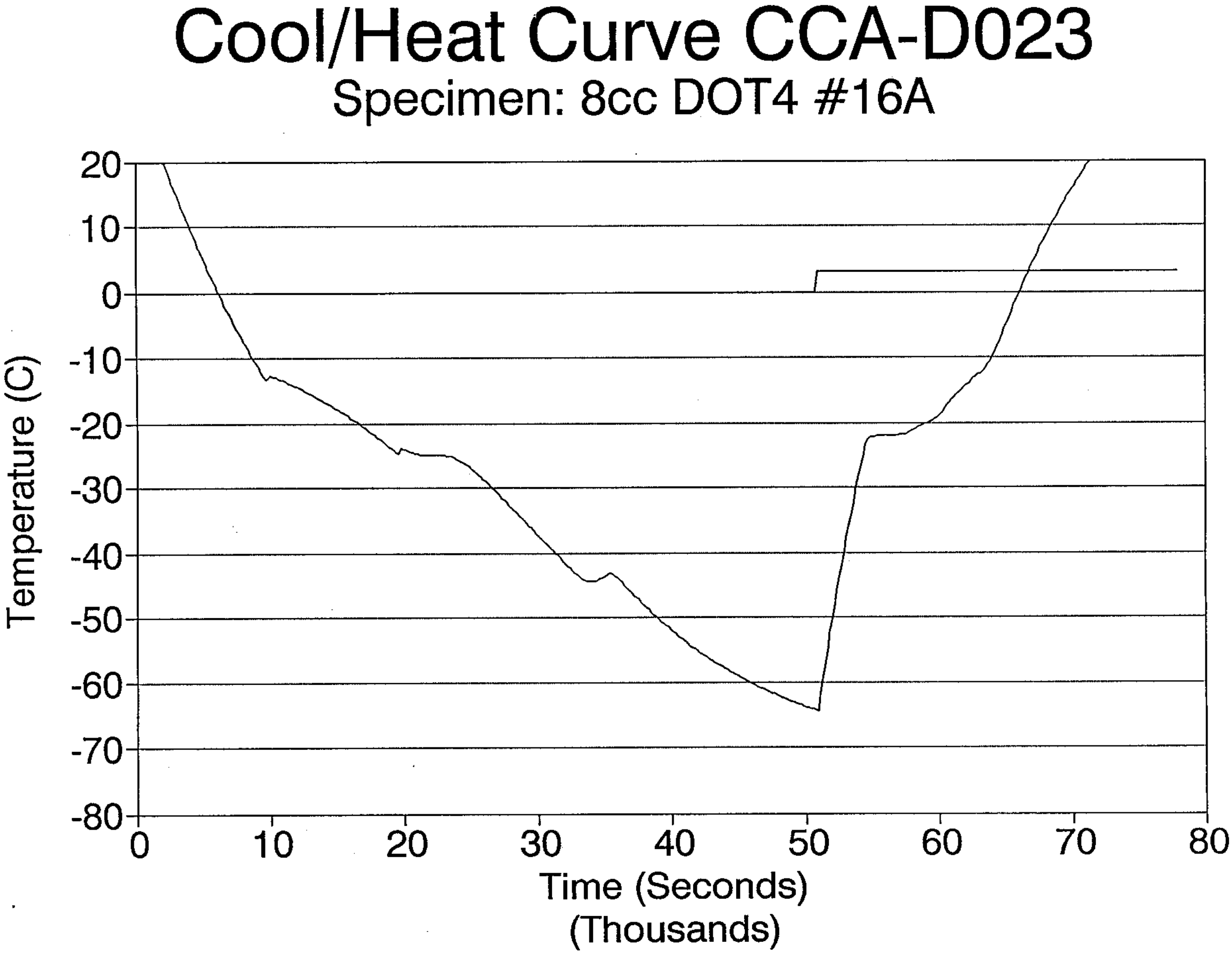


Figure 9: CCA-D023: Cool/Heat Curve for DOT4 #16A.

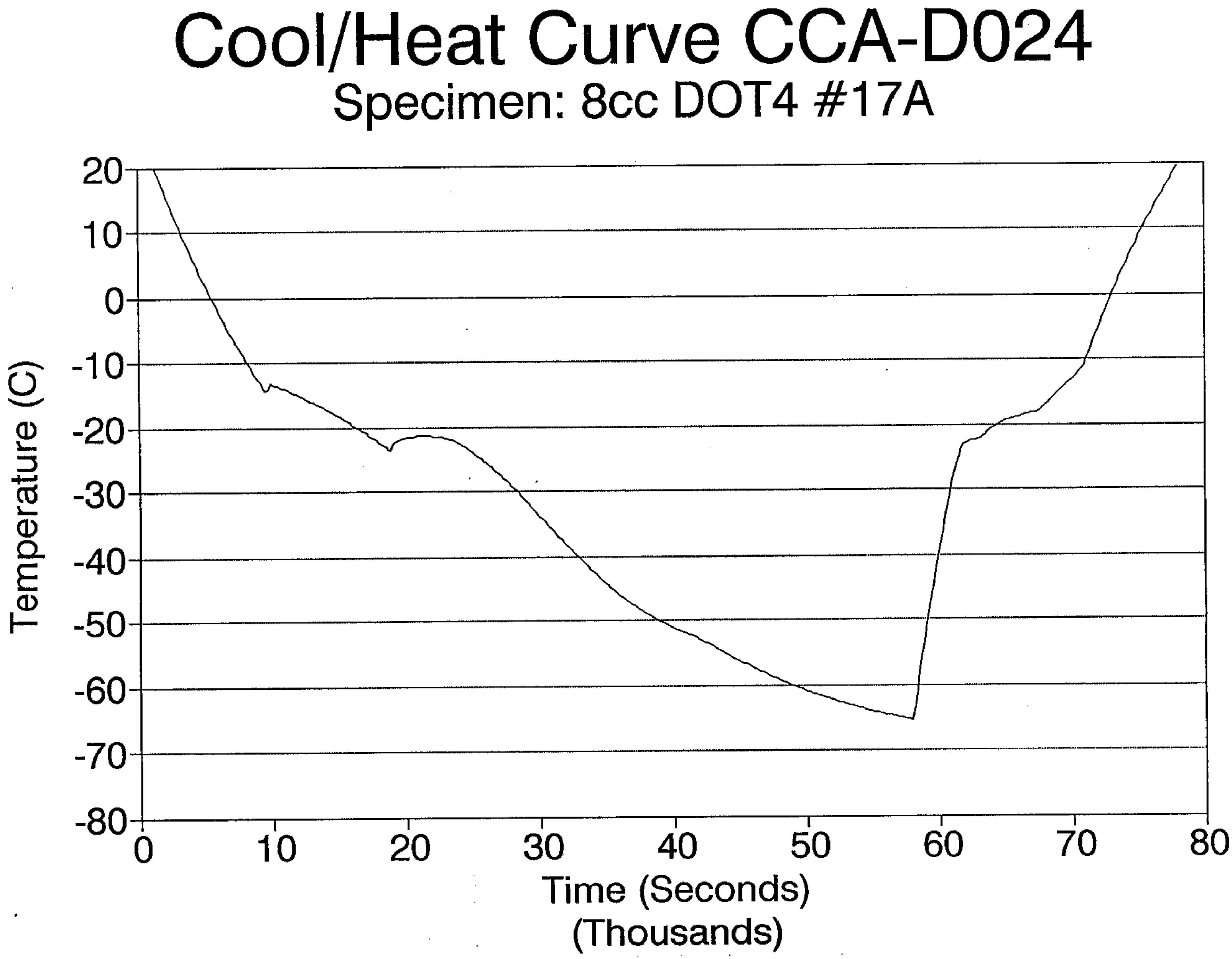


Figure 10: CCA-D024: Cool/Heat Curve for DOT4 #17A.

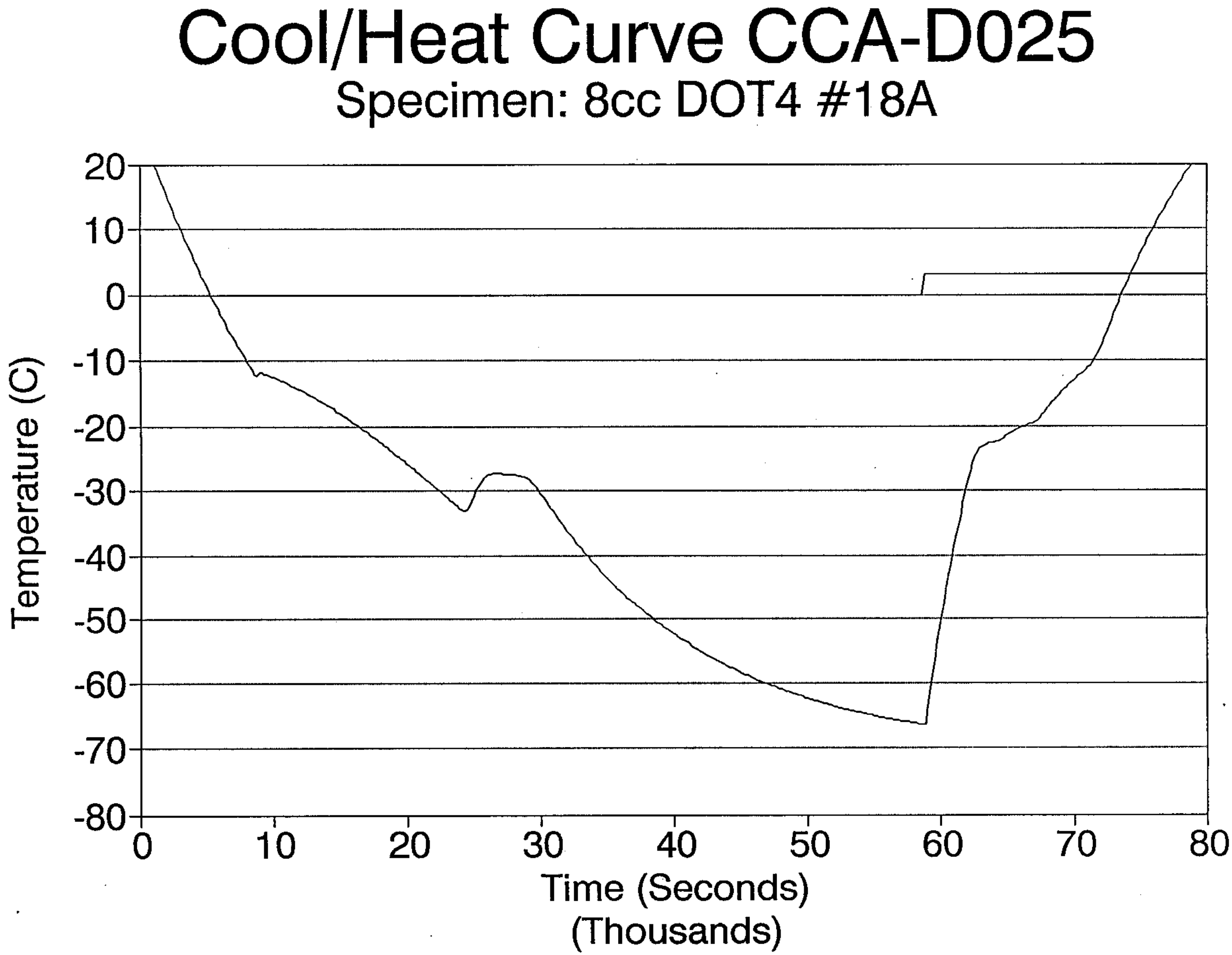


Figure 11: CCA-D025: Cool/Heat Curve for DOT4 #18A.

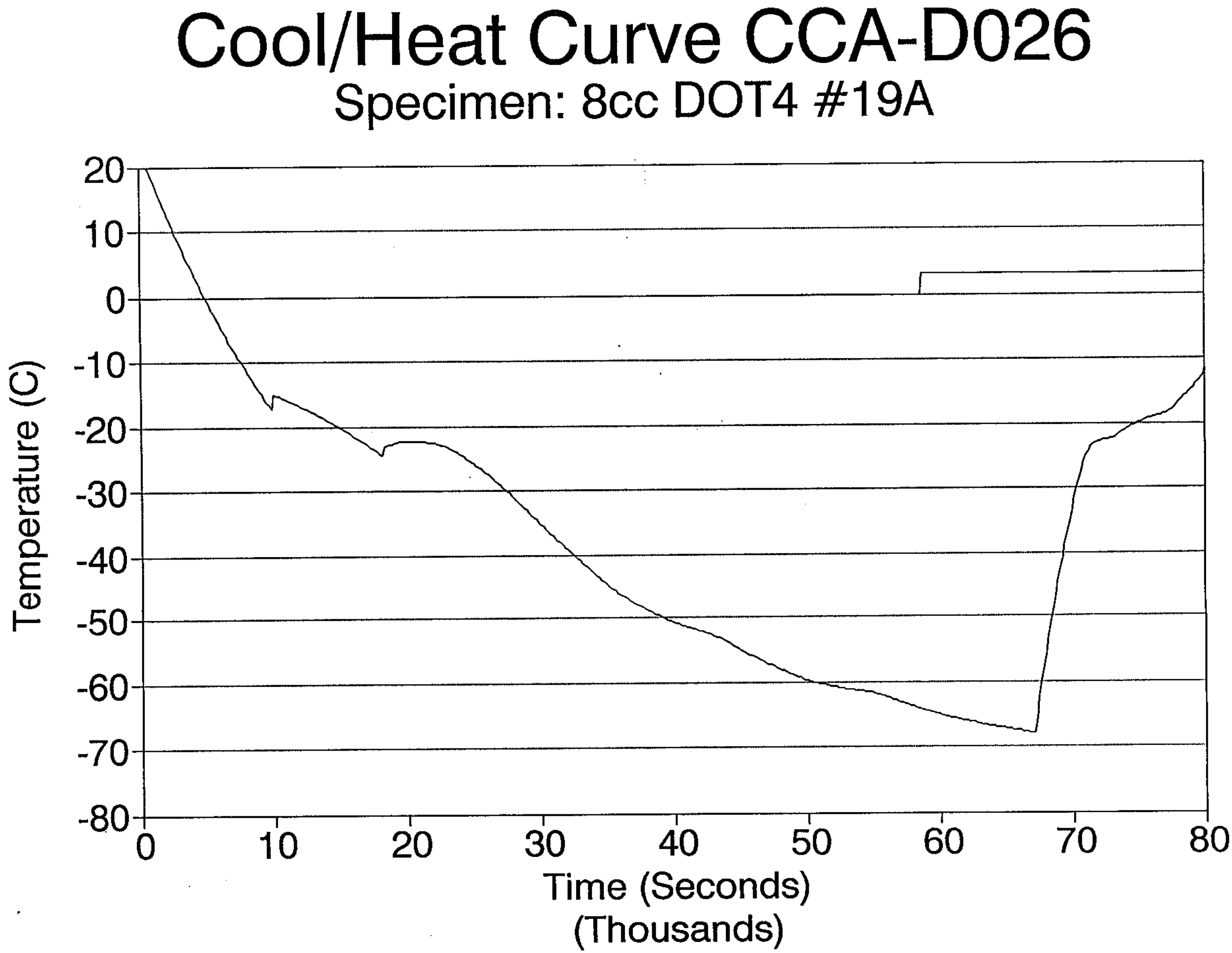


Figure 12: CCA-D026: Cool/Heat Curve for DOT4 #19A.

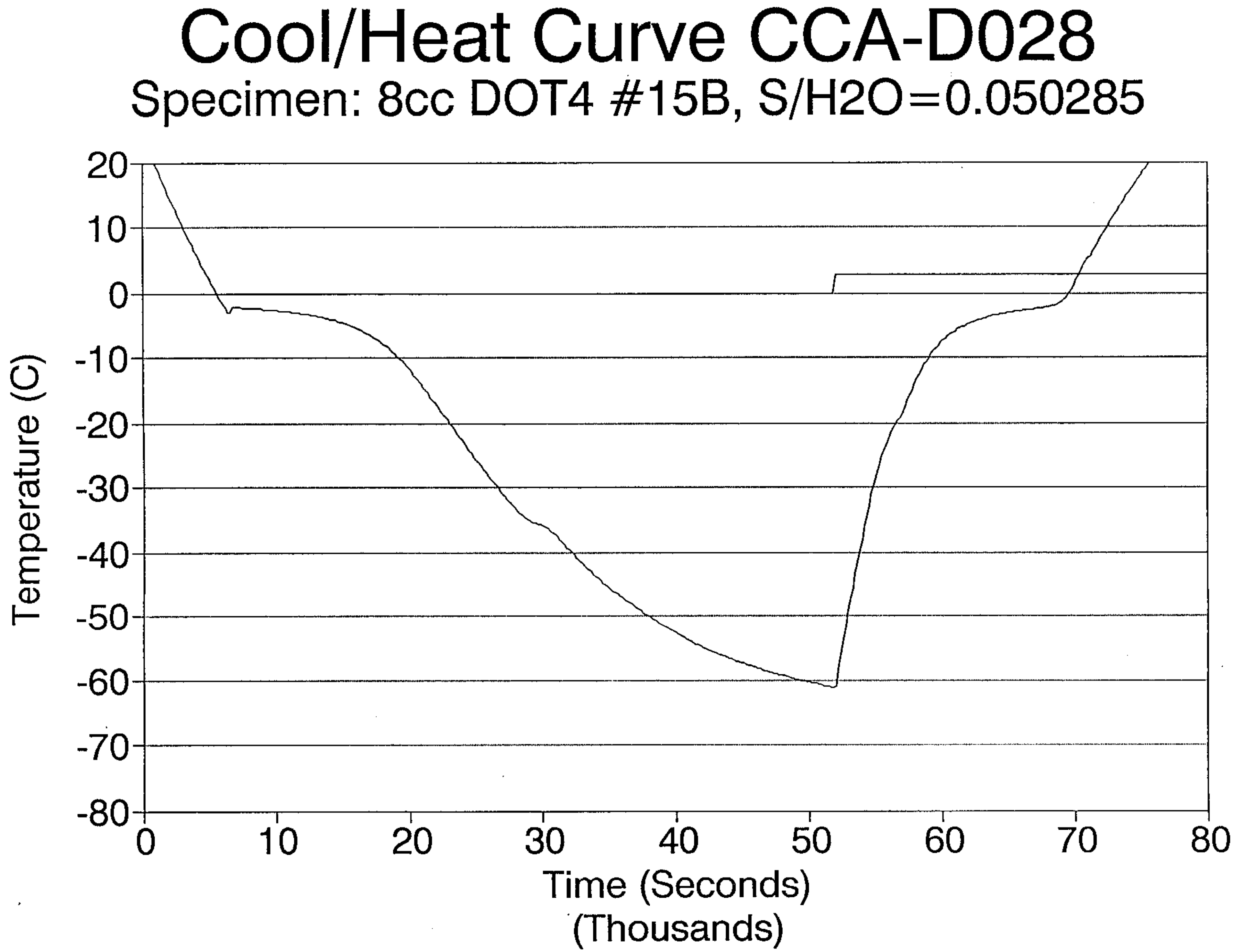


Figure 13: CCA-D028: Cool/Heat Curve for DOT4 #15B.

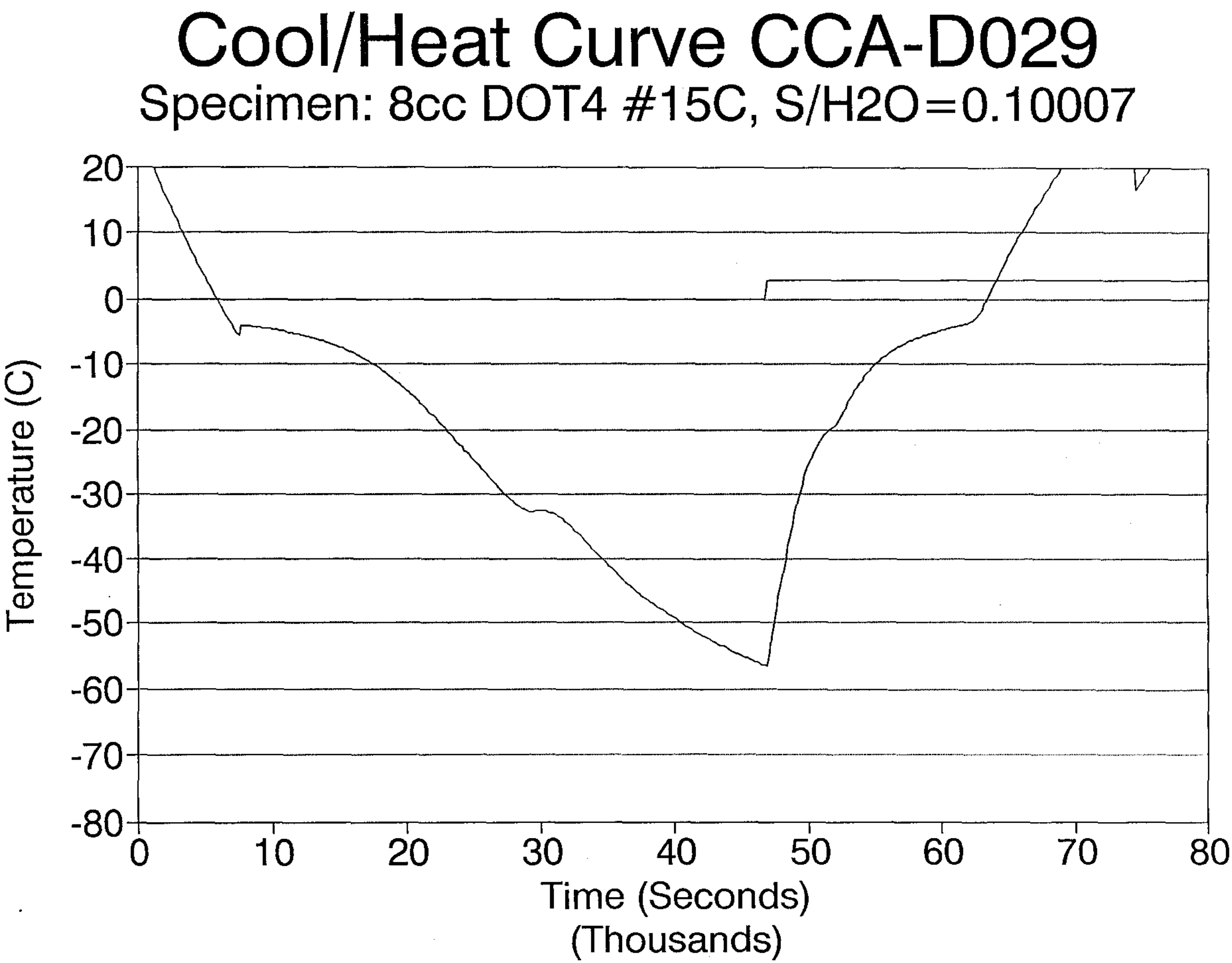


Figure 14: CCA-D029: Cool/Heat Curve for DOT4 #15C.

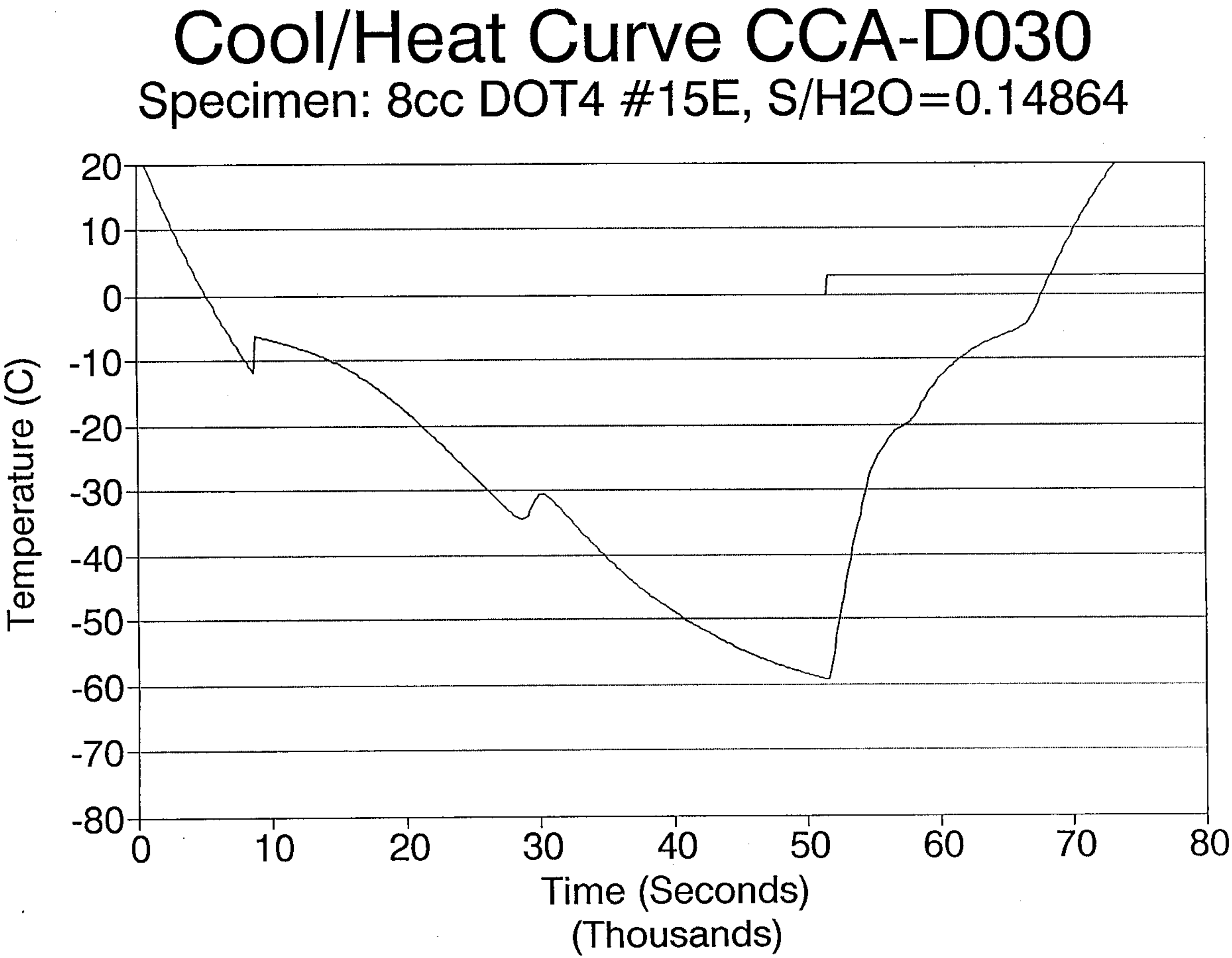


Figure 15: CCA-D030: Cool/Heat Curve for DOT4 #15D.

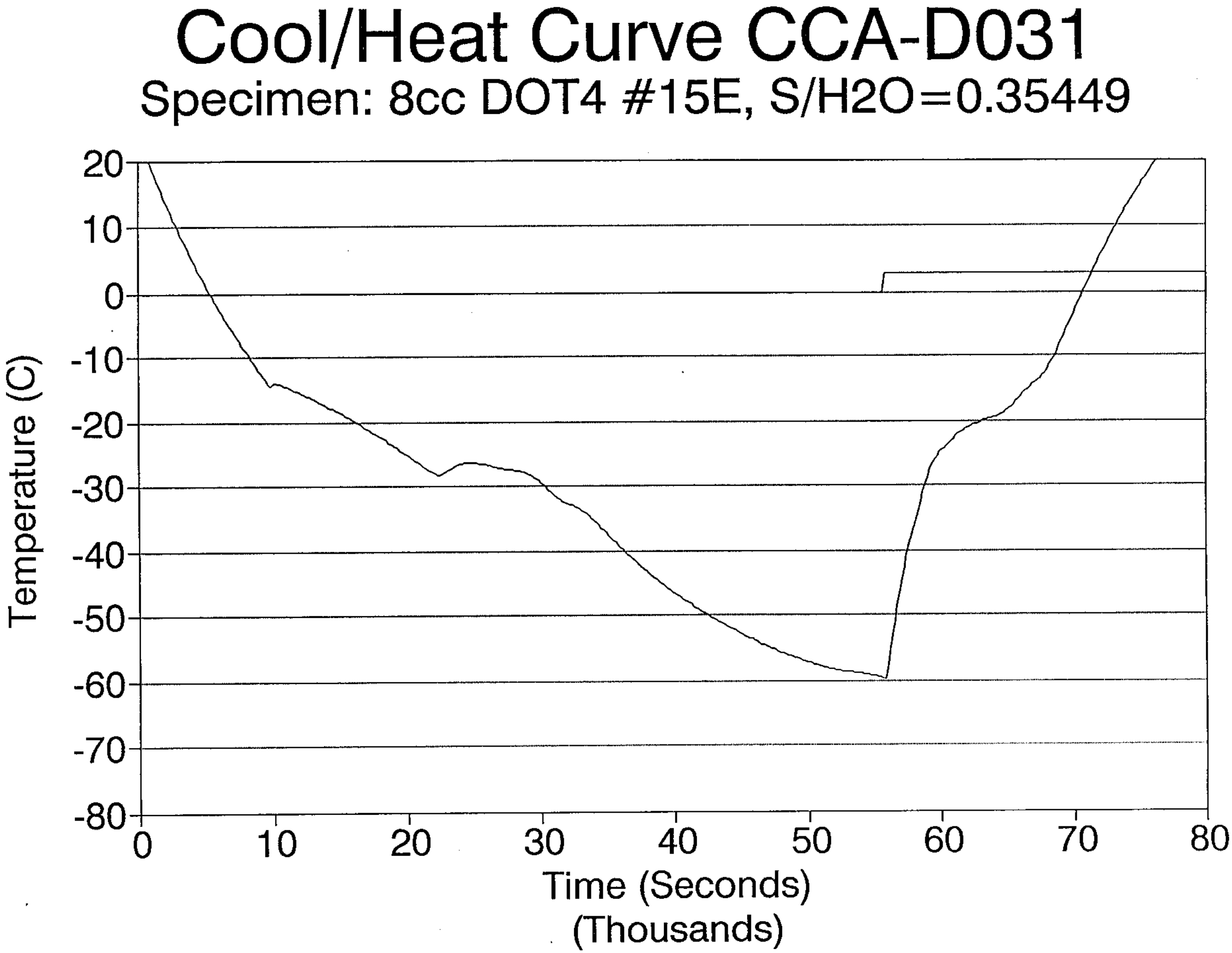


Figure 16: CCA-D031: Cool/Heat Curve for DOT4 #15E.

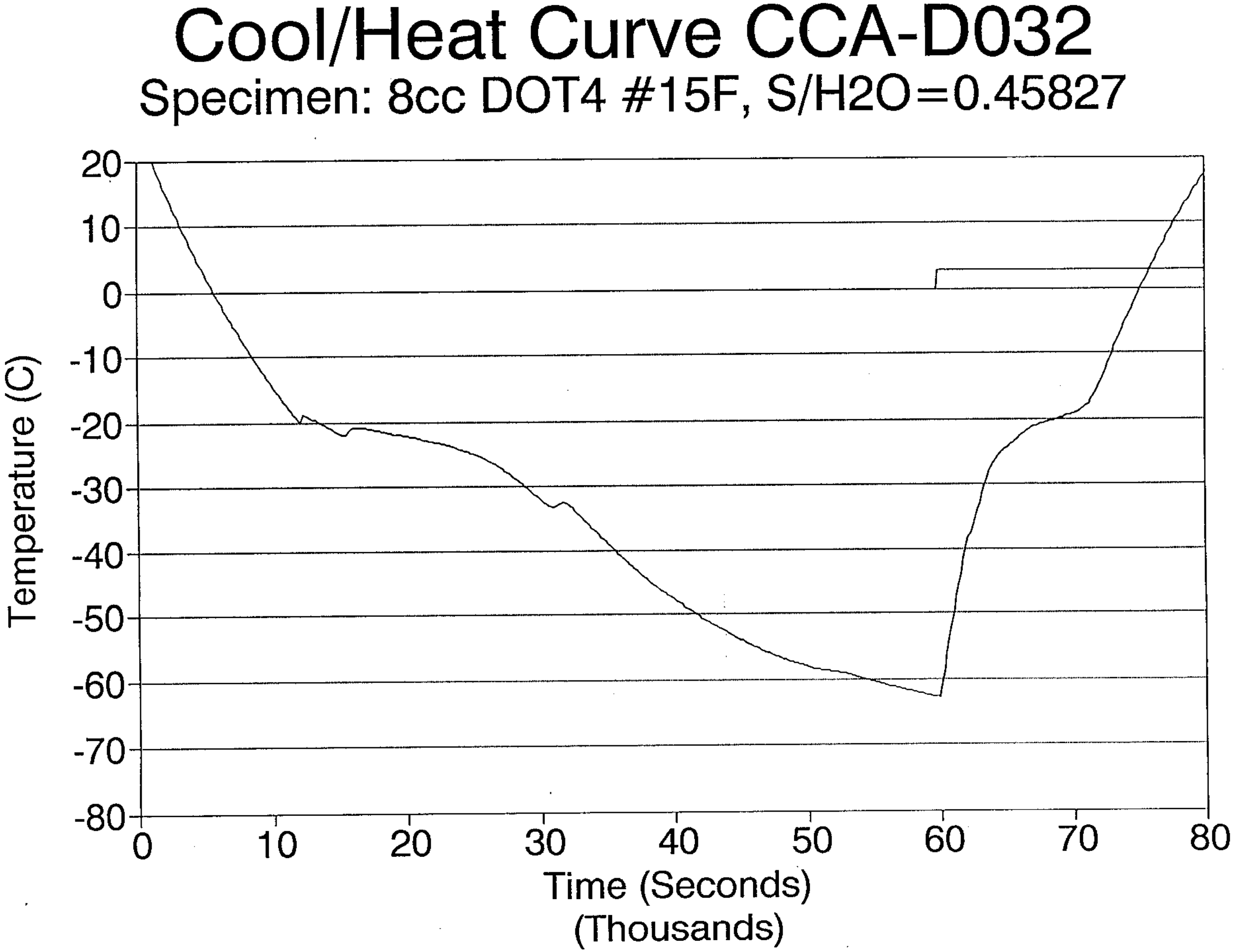


Figure 17: CCA-D032: Cool/Heat Curve for DOT4 #15F.

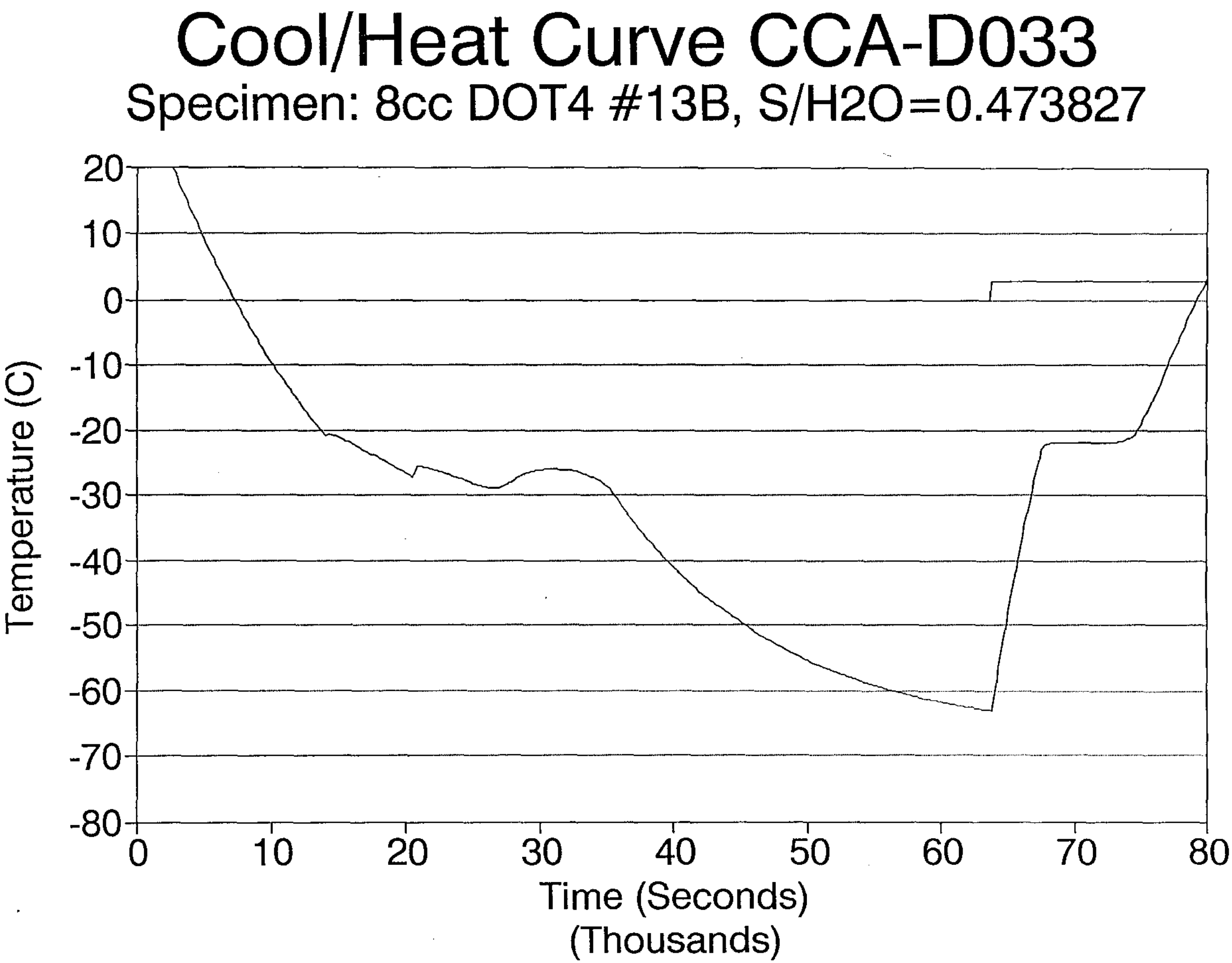


Figure 18: CCA-D033: Cool/Heat Curve for DOT4 #13B.

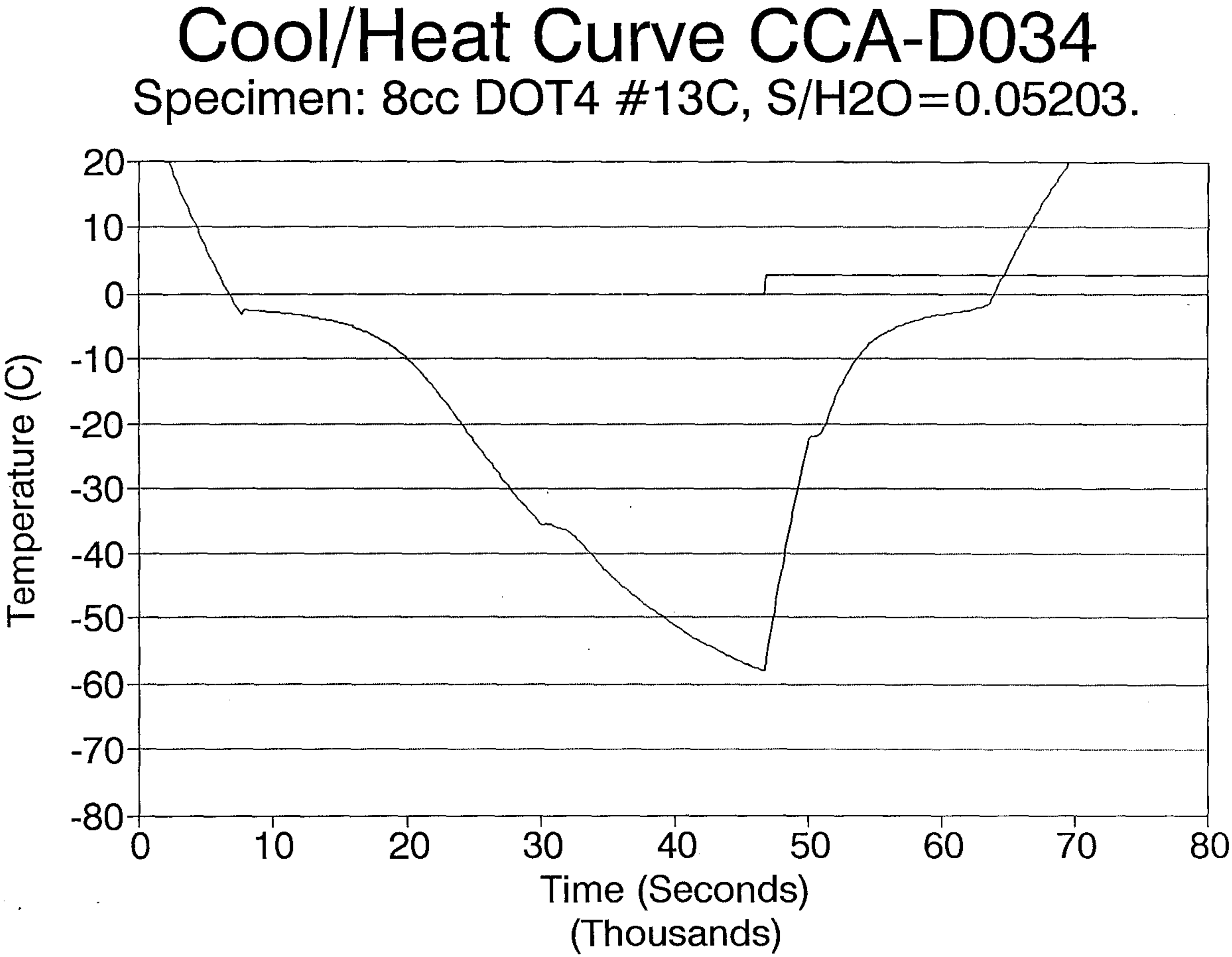


Figure 19: CCA-D034: Cool/Heat Curve for DOT4 #13C.

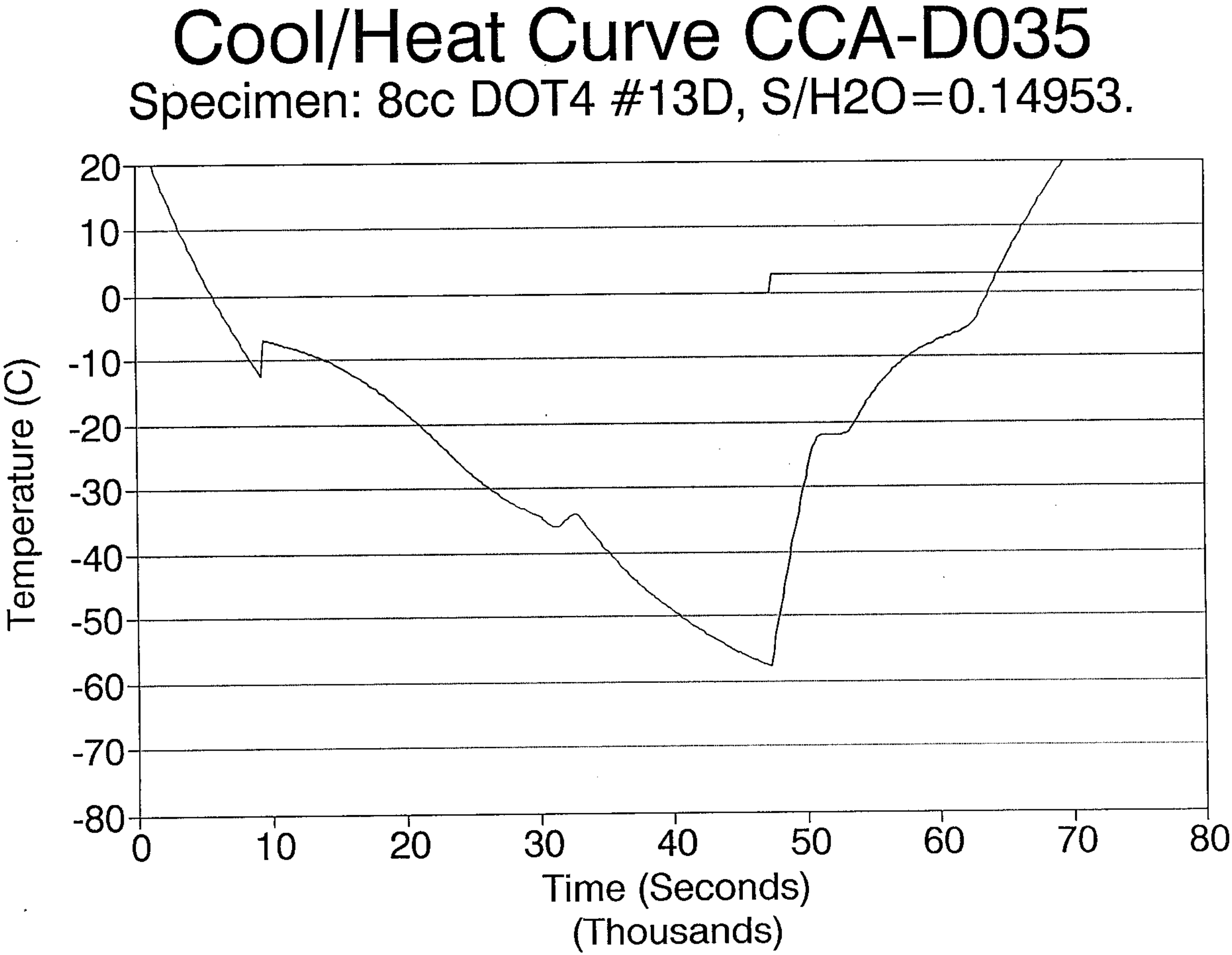


Figure 20: CCA-D035: Cool/Heat Curve for DOT4 #13D.

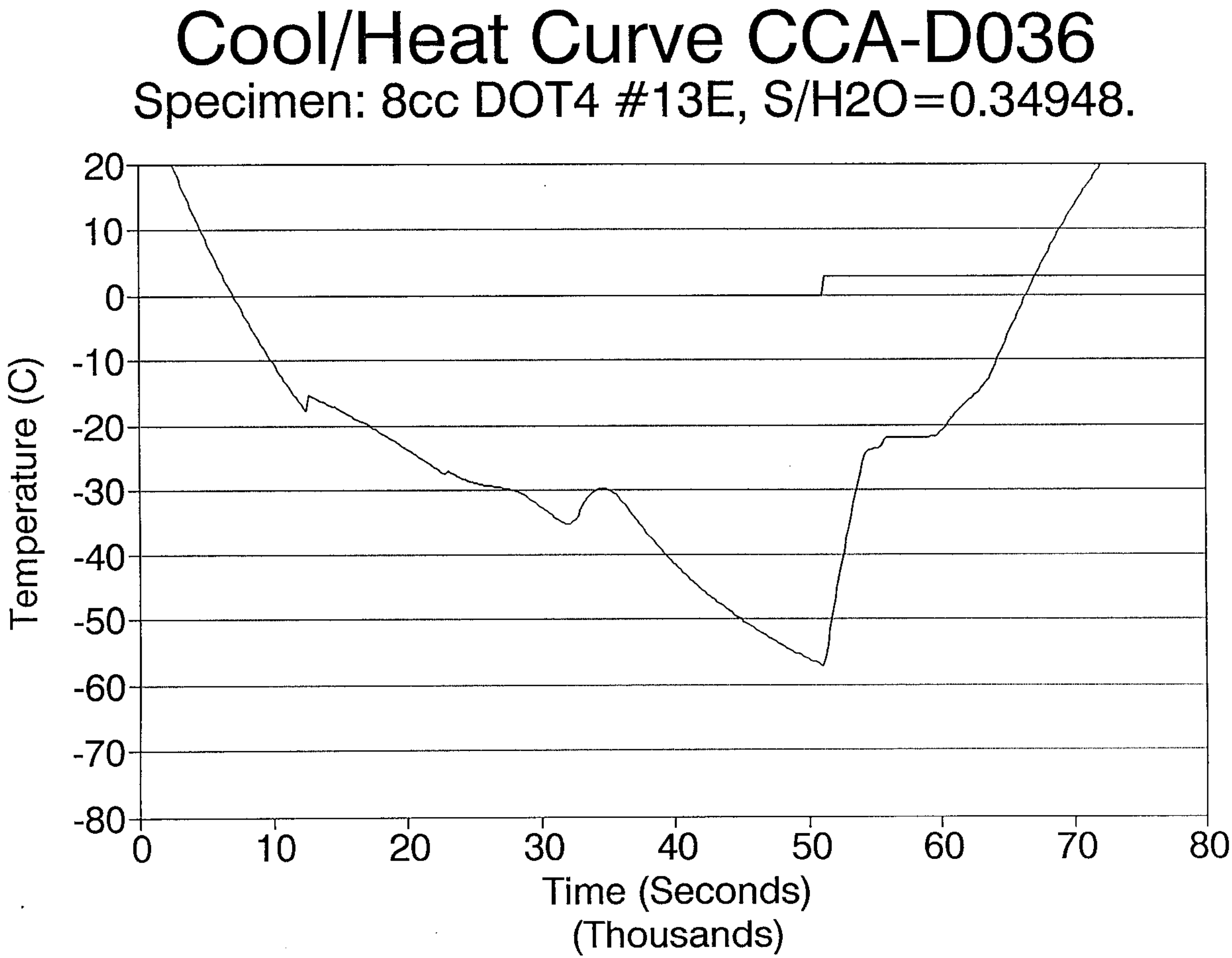


Figure 21: CCA-D036: Cool/Heat Curve for DOT4 #13E.

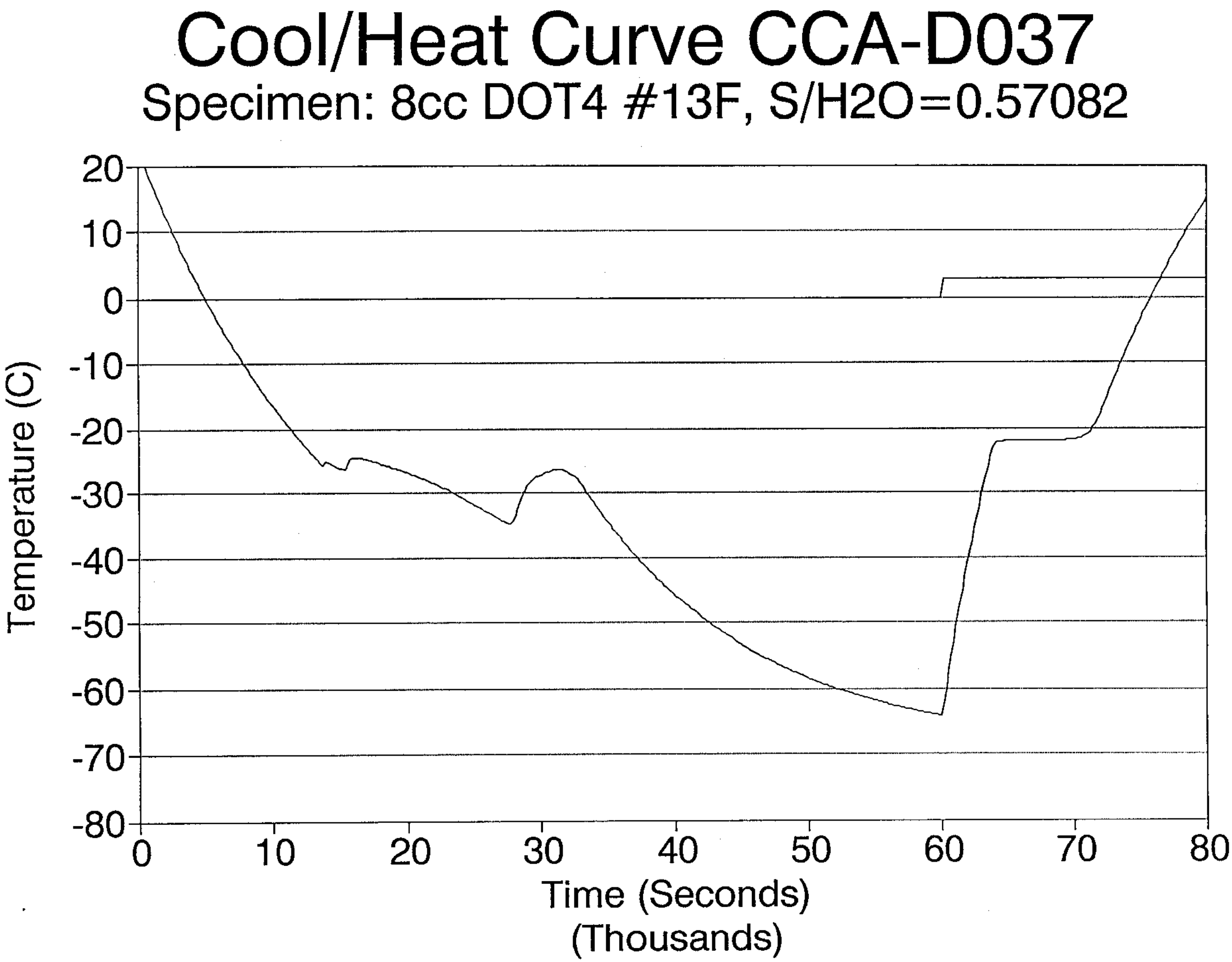


Figure 22: CCA-D037: Cool/Heat Curve for DOT4 #13F.

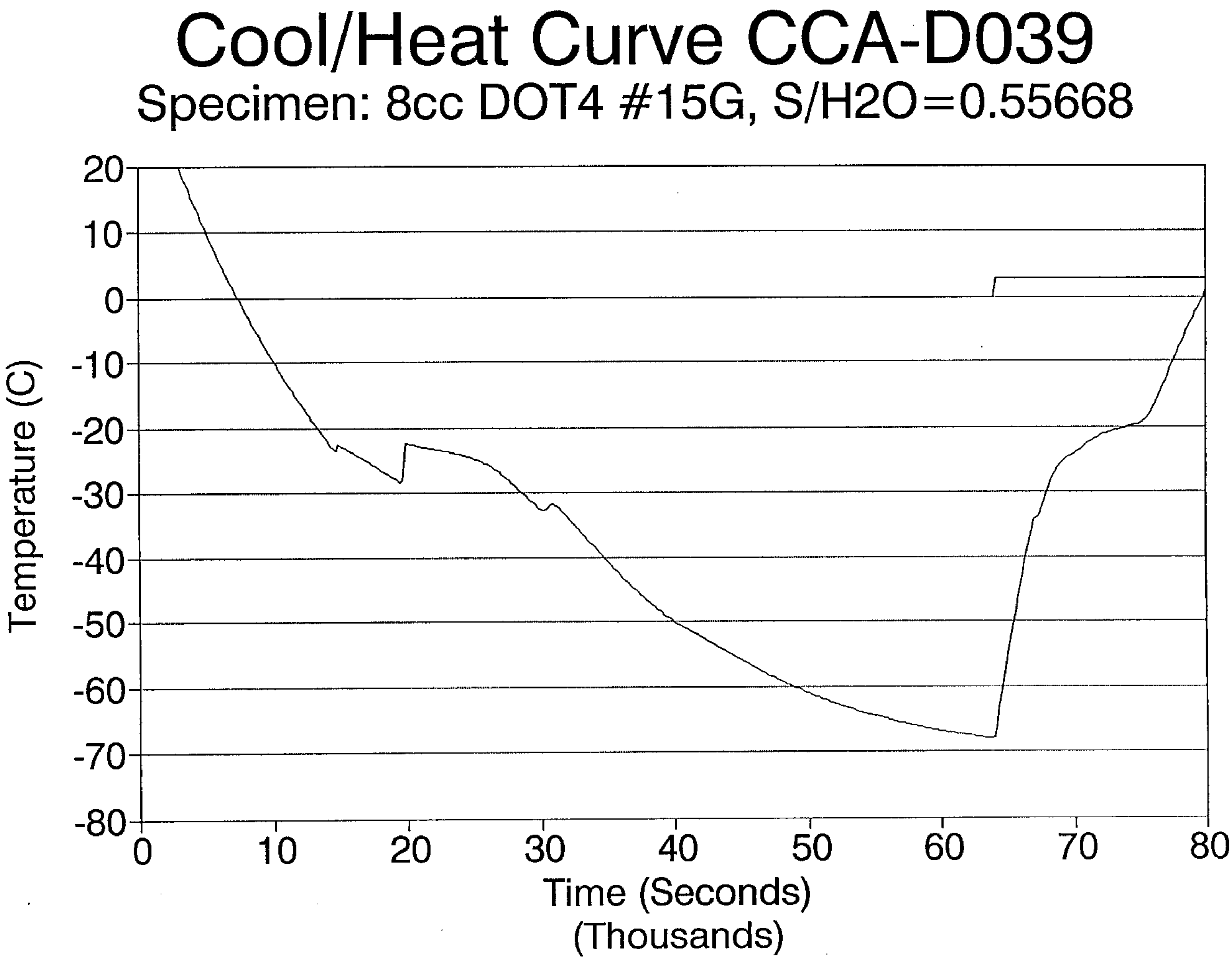


Figure 23: CCA-D039: Cool/Heat Curve for DOT4 #15G.

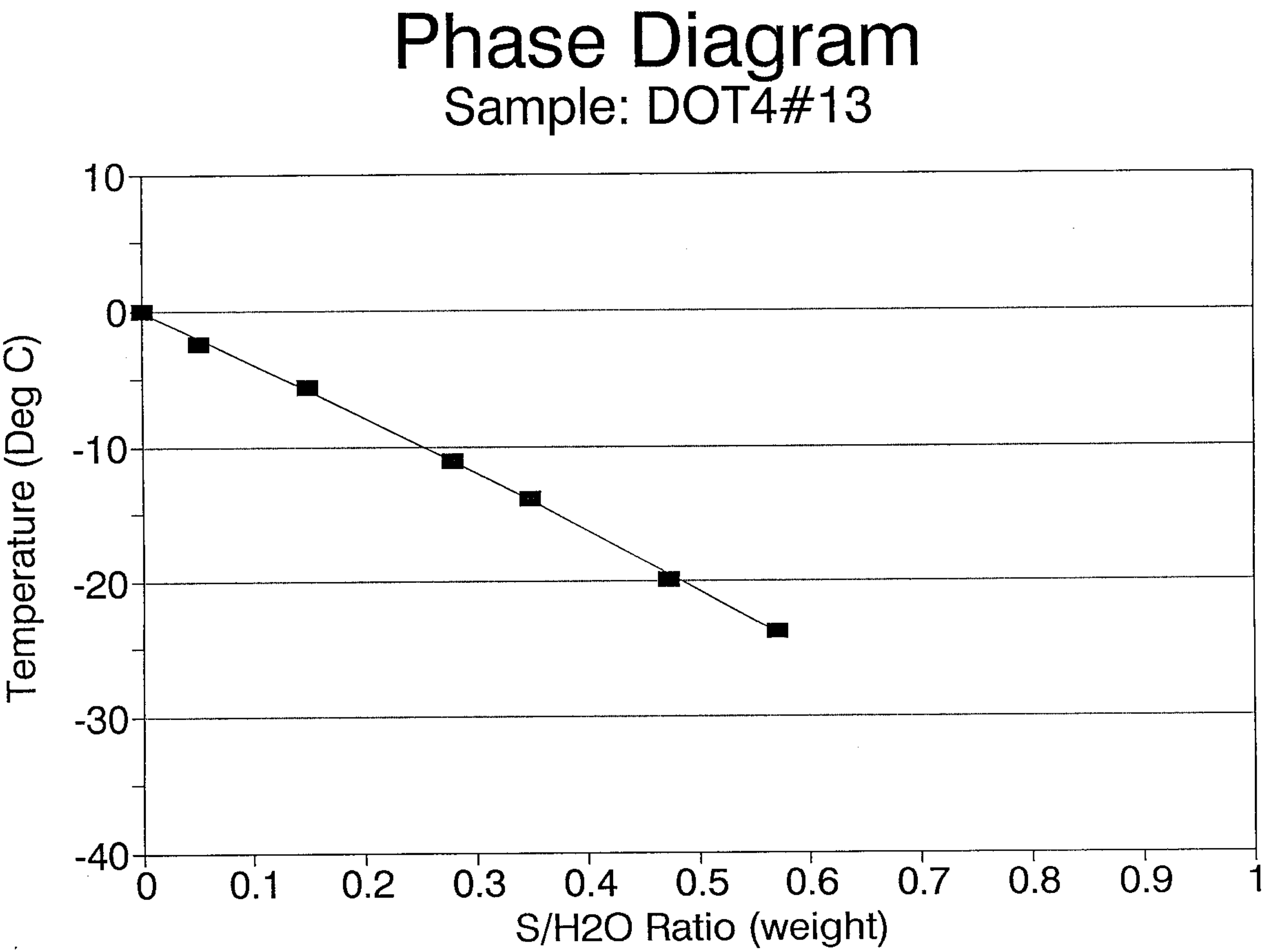


Figure 24: Partial Phase Diagram for Sample 3 of Batch #1.

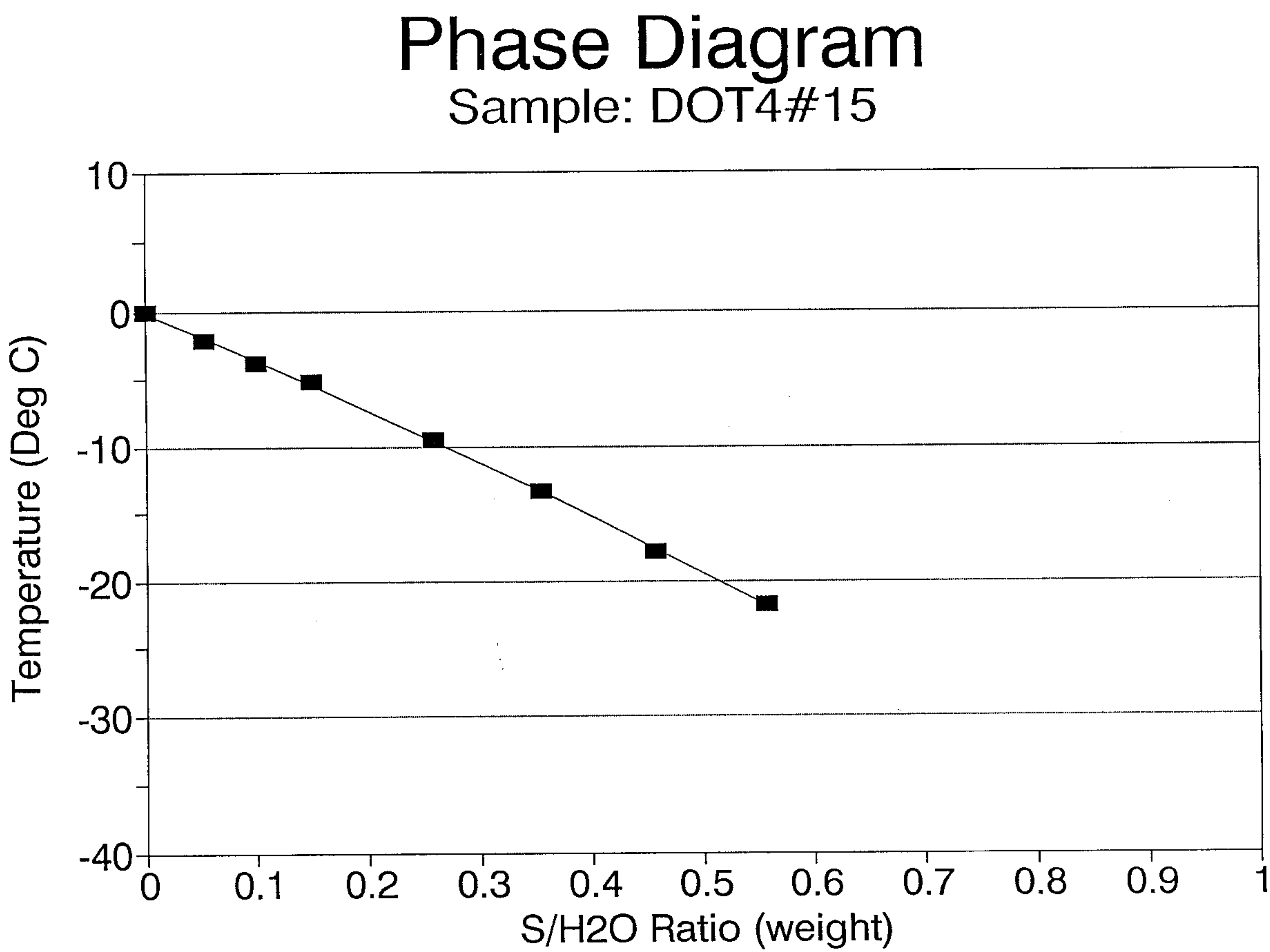


Figure 25: Partial Phase Diagram for Sample 5 of Batch #1.

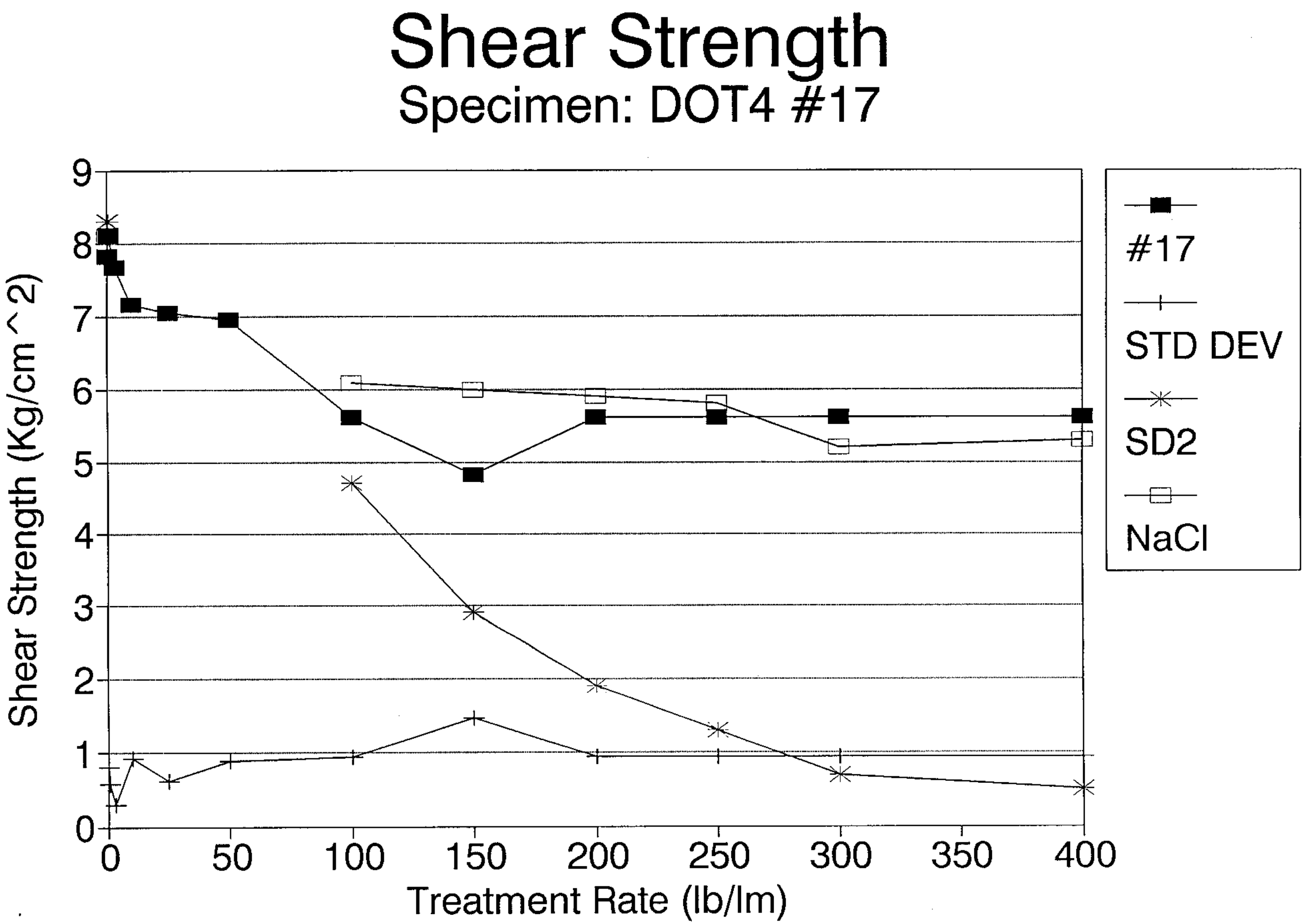


Figure 26: Shear Strength versus Treatment Rate for DOT4 #17.

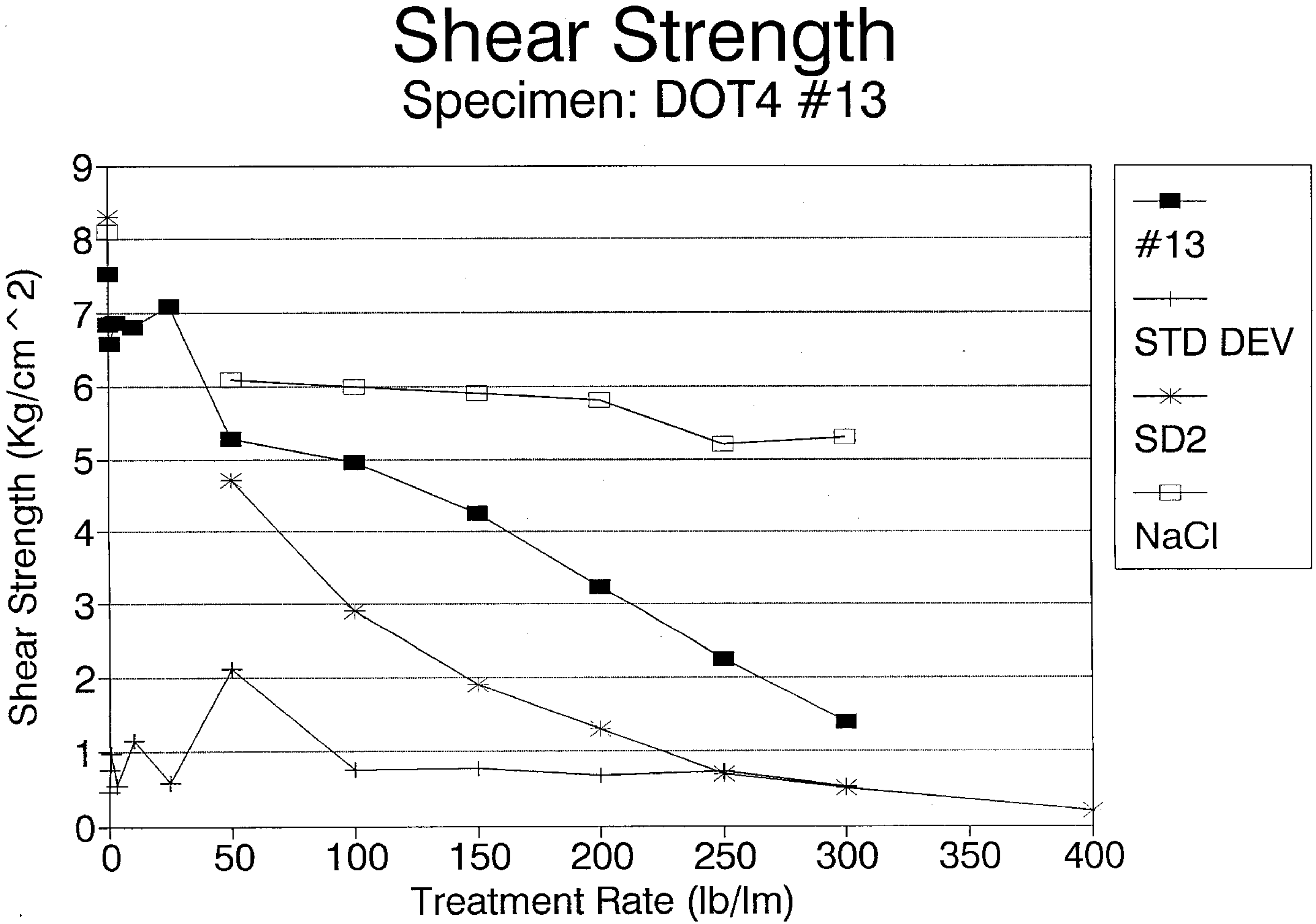


Figure 27: Shear Strength versus Treatment Rate for DOT4 #13

Originally, it was intended to make penetration measurements for salt samples DOT4 #13, DOT4 #15, DOT4 #17, and NaCl for comparison. Because of the performance of sample DOT4 #17 in the shear strength tests, it was not used in the penetration tests.

Each salt specimen used had a mass of 6.5 $\pm$ 0.2mg. The results of the test are shown in Figure 28. Ice column 1 had only red dye placed on it as a check of the effect of the dye itself; as can be seen, there was no penetration by the dye. Columns 2, 5, and 8 had NaCl, columns 3, 6, and 9 had DOT4 #13, and columns 3, 7, and 10 had DOT4 #15. Allowing for parallax and the starting level, NaCl produced a penetration of up to 6mm, DOT4 #13 penetrated up to 2mm, and DOT4 #15 also penetrated by 2mm. It was found that all the penetration which occurred did so in the first 15 minutes of the test.

To obtain greater penetration, it appears that larger salt crystals are needed. Ashworth & Associates would be pleased to perform a further test of penetration at no additional charge if suitable salt specimens can be provided.

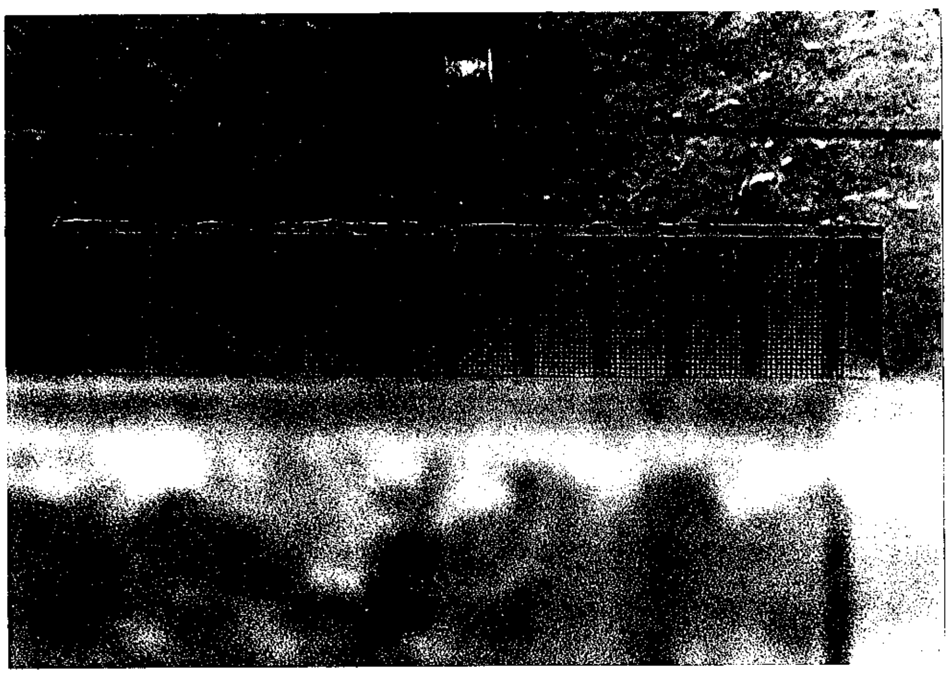


Figure 28: Ice Penetration Test.

APPENDIX A

COOLING CURVES FOR BATCH #0 SAMPLES

These curves were obtained for the seven samples (DOT4 #01 through DOT4 #07) provided for preliminary testing. When these test were taken, automatic stirring and data acquisition were not available.