PART III

SILICA FOULING BY GEOTHERMAL WATERS

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1. INTRODUCTION

In recent years the world-wide interest in geothermal energy has been stimulated by ever increasing costs of conventional fuels. Countries with established means of utilising geothermal resources have expanded their facilities, while elsewhere in the world, various geothermal projects are being investigated. This increased activity has brought to the forefront a problem of long standing in geothermal engineering; that of deposition and fouling. Presently, geothermal waters containing useful energy are being discorded because of the problem. Moreover, high temperature geothermal areas remain untapped because of potential difficulties with deposition and fouling. The problem of fouling may be described as the major constraint on the efficient and environmentally acceptable use of geothermal resources.

Two main types of naturally occurring geothermal areas exist; steam and water dominated[F]. The water dominated areas may be divided into high and low temperature areas, depending on the reservoir temperature. High temperature areas are those with reservoir temperature > $150^{o}C$ and low temperature areas < $150^{o}C$. However, the actual reservoir temperatures are usually $200\text{-}300^{o}C$ and $\sim 100^{o}C$, respectively. There are only water dominated areas in Iceland[D].

Low temperature areas have been used extensively for district heating and horticultural purposes in Iceland since the late 1920s. No major difficulties have been experienced with the utilisation of these areas, except for the usual corrosion problems of any water distribution system. High temperature areas have been explored in Iceland since the 1960s and are now used for the generation of electricity and industrial drying. The problem of deposition and fouling is limited to the high temperature areas. Although the emphasis of the present study is on Icelandic areas, the discussion is equally relevant to similar areas in the United States, New Zealand, Japan, Mexico and elsewhere.

The problem of deposition and fouling may be illustrated by considering what happens when geothermal waters flow upwards through boreholes, to be utilised at the surface. A borehole, drilled in a high temperature area, may be 2000 m deep and discharge up to 100 k/s of a steam/water mixture. The reservoir fluid may be water or brine. The hot fluid at the reservoir base contains dissolved minerals according to temperature-pressure equilibria with the rock[1]. The hot water contains silica derived from the mineral equilibria with quartz.

When the geothermal fluid flows in a borehole, it will flash and form a steam/water mixture. The steam formation and the associated cooling will supersaturate the water with respect to quartz and approach or exceed the solubility of amorphous silica. Field observations indicate that deposition of silica starts when the fluid becomes supersaturated with amorphous silica. This may occur is the borehole or surface pipelines and equipment. In most cases, the deposition process is rapid and gives rise to highly adherent silica deposits, not easily removed by chemical or mechanical means. Silica is the major constituent of most deposits from geothermal waters and brines.

Until recently, only limited information was available on deposition and fouling by geothermal waters. An early study of the problem was that of Sigurgeirsson(2) in a short report to the Icelandic Research Council in 1945. In 1975, Lombard(4) and Wahl and Yen(24) studied the fouling behaviour of geothermal brines and Owen(3) reviewed the chemical aspects of silica deposition. Recent papers on geothermal energy by Axtmann and Peck(5) and Wehlage(6), have stressed the importance of heat transfer technology in geothermal engineering.

2. SILICA IN WATER

The amount of silica in high temperature geothermal waters is governed by the solubility of quartz(7,8). The solubility increases with temperature and is given by the expression(9):

$$c = 48.3 \times 10^3 \exp\left(\frac{-2463}{T}\right) \qquad \ldots. (1)$$

where c is the concentration of silica (SiO_2) in mg/kg and T the absolute temperature ^{o}K. When geothermal waters saturated with silica in equilibrium with quartz are subjected to sudden cooling, no deposition occurs until the water becomes saturated with respect to amorphous silica(8,10-12). The solubility of amorphous silica in water is given by the expression:

$$c = 15.1 \times 10^3 \exp\left(\frac{-1354}{T}\right) \qquad \ldots. (2)$$

These expressions were derived from data given by Volosov et al(9) and are applicable at neutral pH. At 25^{o}C, 100^{o}C and 250^{o}C the solubility of quartz is 12, 65 and 435 mg/kg and that of amorphous silica 161, 400 and 1134 mg/kg, respectively. The solubility of silica in steam has been given by Martynova et al[13].

The principal form of dissolved silica in water in monosilicic acid H_4SiO_4 or $Si(OH)_4$, which is a weak acid and therefore practically undissociated in neutral solutions[14]. In basic solutions when pH > 9, silicic acid dissociates and increases the total solubility considerably[15]. The dissolution of silica in water can be expressed by the hydration reaction:

$$SiO_2\ (s) + 2H_2O \rightleftarrows H_4SiO_4 \qquad \ldots. (3)$$

where solid silica is converted to monosilicic acid[16,17].

Excess silicic acid in geothermal waters, supersaturated with amorphous silica, will not only deposit, but also polymerise[11,16-18]. The polymerisation process is essentially one of dehydration[16]; the reverse of Equation 3. In acid solutions polymerisation results in the formation of silica gel while in neutral and alkaline solutions polymerisation gives rise to negatively charged colloidal particles[16,17]. Geothermal waters are usually neutral or basic[10]. Both dissolved and colloidal species of silica may therefore contribute to deposition and fouling by geothermal waters.

The solubility of silica in water can be lowered considerably by the addition of trace amounts of aluminium and iron and other trivalent ions[18-21]. It seems probable that the formation of a very insoluable aluminium silicate on the surface of amorphous silica simply prevents the underlying silica from passing into solution[16]. The amount by which the solubility of silica is reduced, depends on the pH value. The solubility is only reduced by an appreciable amount when the pH is in the range 4-10 with a minimum solubility at a pH value of about 9[18,20].

Iler[16,17], McKeague and Cline[22] and Owen[3] have all reviewed the chemistry of silica in water. Imhoff and Burkardt[23] have discussed crystalline compounds observed in water treatment, including silica.

3. EXPERIMENTAL WORK

Simulated heat exchanger tubes and a plate heat exchanger were used to study the fouling characteristics of two geothermal fluids. The work was carried out at Svartsengi and Hveragerdi, which are high temperature areas in south-west Iceland[D]. At Hveragerdi the geothermal fluid was of rain water origin, but at Svartsengi the fluid originated from sea water. The solids content of these fluids were low and intermediate(F), respectively. The brine used in the simulated heat exchangers at Svartsengi contained 30,000 mg/kg dissolved solids, of which 580 mg/kg was silica. The Hveragerdi water contained 800 mg/kg dissolved solids, of which 300 mg/kg was silica(E).

Simulated heat exchanger tubes were used at both locations, together with a plate exchanger at Svartsengi. The tube exchangers were 2 m long 12.7 mm OD stainless steel with a 1.5 m cooling jacket 19.1 mm OD. The first 0.5 m acted as an entry section. The wall thickness of all tubes was 1.22 mm. The plate exchanger was an Alfa-Laval P22 exchanger with 13 plates. The heat transfer experiments consisted of circulating the geothermal fluids through the exchangers and cooling by cold mains water. All flowrates were maintained constant. Inlet and outlet temperatures of hot and cold streams were measured. Because silica in water exhibits normal solubility - ie the solubility increases with temperature - deposition occurred as the geothermal fluids were cooled. The data reduction consisted of calculating the fouling resistance $R_f (kW/m^2\ {}^{o}C)^{-1}$ with time(E).

Two results from the tubular exchangers were obtained at Svartsengi in 4 weeks and one result from the plate exchanger in 6 weeks. The exchangers fouled much more slowly than anticipated. At Hveragerdi arrangements were made for longer experimental periods. Three tubular exchangers were operated for three months.

Run No 1 at Svartsengi was used to evaluate the heat transfer performance of the clean tubular exchangers. The two tubular fouling experiments at Svartsengi, No 2 and No 3, were operated at Reynolds number for the brine flow of 44,000 and 39,000 respectively. The fouling resistance R_f is plotted with time in Figure 1. The plate exchanger experiment, No 4, is also plotted in Figure 1. The fouling resistance of the plate and tubular exchangers increases linearily with time. If the initial fouling resistance is taken as zero, the tubular results suggest a fouling resistance of about 0.08 $(kW/m^2\ {}^{o}C)^{-1}$ in 800 hours, for both runs. The corresponding values for the plate exchanger were about 0.1 $(kW/m^2\ {}^{o}C)^{-1}$ in 1000 hours. Assuming a linear relationship $R_f = kt$ where $R_f = 0$ at $t = 0$, the constant becomes $k = 10^{-4}$ for both the tubular and plate results at Svartsengi. The fouling data obtained at Svartsengi may therefore be expressed by the approximate relationship:

$$R_f = 10^{-4}\, t \qquad \text{.... (4)}$$

The fouling results obtained at Hveragerdi were quite different from those at Svartsengi, as shown in Figures 2-4. The fouling resistance in Runs 1 and 2, at Reynolds number 44,000 and 23,000 respectively, assumed a spoon-like shape. The spoon fouling curves probably result from the silica deposit surface being rippled in character. Rippled deposits are discussed in detail in Part IV of the Thesis. The fouling resistance of Experiment 3 was not spoon shaped; the Reynolds number was only 7300. To illustrate the sort of experimental measurements and calculated values obtained in the present fouling studies, the data for Run No 2 at Hveragerdi is given in the Appendix.

Silica deposits from the exchangers at Svartsengi and Hveragerdi were examined for composition, structure and appearance. The main feature of the deposits was their amorphous structure as determined by X-ray diffraction. Imhoff and Burkardt[23] have discussed both crystalline and amorphous silica deposits. The Svartsengi plate exchanger deposit consisted of 87 per cent silica while a deposit removed from a large plate exchanger at Hveragerdi, operating under similar conditions as the tubular exchangers, consisted of 60 per cent silica. Scanning electron micrographs showed the Svartsengi and Hveragerdi deposits to be different in appearance. See Figure 5. The Svartsengi tubular deposits (a) were globular, evenly distributed and apparently dense. The plate exchanger deposit (b) was rough and more porous than the tubular deposit. The Hveragerdi tubular deposit (c) was rough and rippled.

4. DISCUSSION

The experimental results show two different fouling characteristics; linear and spoon-like. The shape of most fouling curves is dependent on three main effects; deposit thermal insulation, tube diameter reduction and deposit roughness. In the tubular exchangers the diameter effect was probably negligible, while in the plate exchanger it may have influenced the heat transfer performance in the latter part of the experimental period[E]. The roughness effect played an important role in the Hveragerdi results, because of the rippled deposit structure[25], but not at Svartsengi. Hence the linear and spoon-like fouling curves.

For deposition and fouling to occur, there must be a deposition driving force; usually some concentration difference. The deposition driving force may be illustrated by considering the temperature conditions in an exchanger. Table 1 shows the average temperature conditions in the fully turbulent runs at both locations(E). An examination of this table shows the deposition

TABLE 1 - Temperature Conditions in Exchangers

Run No	$\overline{T}_{in}$ (^oC)	$\overline{T}_{out}$ (^oC)	T_{sat} (^oC)	$\overline{T}_{wall}$ (^oC)
Svartsengi 2	90	73	143	32
Svartsengi 3	91	69	143	26
Svartsengi 4*	152	44	140	35
Hveragerdi 1	81	68	74	26
Hveragerdi 2	80	62	74	24

* Plate exchanger

driving force (T_{sat} - $\overline{T}_{wall}$, say) at Svartsengi to be much greater than at Hveragerdi. However, an examination of the fouling curves shows, Figures 1-4, that for the tubular experiments in Table 1 the fouling resistance R_f has a similar value after ∿ 800 hours. Moreover, the fouling resistance of the plate and tubular exchangers at Svartsengi increased at approximately the same linear rate, despite the different temperature and hydrodynamic conditions.

Equation 2 was used to calculate the saturation temperature T_{sat} from the dissolved silica content of the geothermal fluids. The expression was derived from the solubility of amorphous silica in distilled water at neutral pH conditions. Its applicability to geothermal waters has not been tested. Table 1 shows that at Hveragerdi the inlet water was ∿ 5^oC undersaturated. No deposition should therefore occur upstream from the exchangers unless the wall temperature was less than T_{sat}, the saturation temperature. The pH of the Svartsengi and Hveragerdi waters was 7.5 and 9.5 at ∿ 25^oC, respectively(E). Some of the silica at Hveragerdi must therefore have been dissociated, thus increasing the total solubility of silica. However, experience at Hveragerdi has shown that deposition occurs in the pipeline (thermally insulated) carrying the geothermal water at 80-95 ^oC(26). The solubility of amorphous silica in the geothermal water at Hveragerdi may have been lowered by the presence of cations of aluminium and iron; both of which were identified in the silica deposit(E).

At both Svartsengi and Hveragerdi there were probably no colloidal particles in the geothermal fluids that passed through the experimental heat exchangers. There are situations, however, where colloidal silica may be present. Yangase et al[27] have suggested that colloidal particles are less likely to deposit than dissolved silica. The colloidal chemistry of hydrophobic sols is discussed in Part V, Section 4.3.3 of the Thesis. Colloidal silica in neutral and basic solutions will be negatively charged, probably through the dissociation of surface hydroxyl groups. Because of the negative charge, the particles attract cations and an electric double layer will be formed. The stability and deposition behaviour of the particles will be governed by the pH of the water and the concentration of cations. The particles would be least stable at low pH and high cation concentration. For example, colloidal silica will be less stable in sea water than fresh water, at similar pH values. According to Krauskopf[11], the solubility of amorphous silica in sea water and fresh water is the same. Napper and Hunt[28] have stated that colloidal silica does not necessarily behave according to the classical DLVO-theory on the stability of inorganic hydrosols.

As already stated, the principal form of silica in water is silicic acid. In waters supersaturated with silica the acid may polymerise to form colloidal particles or presumably deposit directly on surfaces; in both cases by a dehydration reaction as expressed by Equation 3 moving from right to left. The dissolved silica content of the outlet brine from the exchangers at Svartsengi was measured (using standard methods) as a function of time at various constant bulk temperatures $< 75^{o}C$. In all instances the dissolved silica content decreased exponentially to an equilibrium value is $\sim$ 1 hour. The polymerisation reaction, dehydration, was therefore slow in comparison to the brine residence time in the exchangers. It could be argued that the deposition reaction must also be slow. If so, the build-up of silica deposits may be controlled by the rate of dehydration of silicic acids. This would explain why different exchanger hydrodynamics and silica concentrations resulted in similar rates of fouling. However, the data are too limited for any firm conclusions to be drawn. Fluoride is known to catalyse the polymerisation of silicic acids in water, and would presumably also catalyse the rate of silica deposition and fouling.

The chemical composition of geothermal fluids may vary extensively from one location to another[1]. Geothermal waters are natural fluids and contain a multitude of species in various concentrations. Because of the many factors that affect silica in water, its deposition and fouling behaviour is rather unknown. Further work is required into all aspects of geothermal silica to understand this major constraint on the utilisation of geothermal resources.

5. CONCLUSIONS

1. Silica deposition and fouling is a major constraint on the efficient and environmentally acceptable use of geothermal resources.

2. The solubility of amorphous silica in water may be lowered by the presence of cations, particularly aluminium and iron.

3. The fouling resistance at Svartsengi increased linearily with time $R_f = 10^{-4}\ t$. The deposits were globular and rough.

4. Rippled deposits were formed at Hveragerdi where the fouling resistance with time curve was spoon-like in shape.

5. The colloidal behaviour of silica may in some instances affect deposition and fouling.

6. The build-up of silica deposits may be controlled by the dehydration of silicic acids.

6. RECOMMENDATIONS FOR FURTHER STUDIES

1. The solubility of amorphous silica in geothermal waters should be determined at different pH values and various cation concentrations. The rate of polymerisation should also be studied.

2. The deposition behaviour of dissolved and colloidal silica should be studied; initially at isothermal conditions. The geothermal fluid could be concentrated to the required value in a suitably controlled flash-separator. To study the deposition of dissolved silica, the fluid could be passed through an isothermal test section immediately. To study colloidal deposition, the fluid could be retained at constant temperature in a tank, long enough for the excess silicic acid to polymerise and form colloids. Then, the fluid could be passed through an isothermal test section. The test section would be a long, well insulated tube. The amount deposited could easily be determined by cutting off a short section from the downstream end of the tube. The cut-off piece could be weighed before and after cleaning. The effect of diffusion on deposition would

be studied at different flowrates. The effect of concentration would be obtained, to some extent, from the degree of flashing. The effect of reaction (dehydration) would be indicated from runs at chemical conditions resulting in different rates of polymerisation.

NOMENCLATURE

c	:	Concentration (mg/kg)
k	:	Constant
R_f	:	Fouling resistance $(kW/m^2\ ^oC)^{-1}$
T	:	Temperature (^{o}K)
$\overline{T}_{in}$	:	Average inlet temperature (^{o}C)
$\overline{T}_{out}$	:	Average outlet temperature (^{o}C)
T_{sat}	:	Saturation temperature (^{o}C)
$\overline{T}_{wall}$	:	Tube wall temperature (^{o}C)

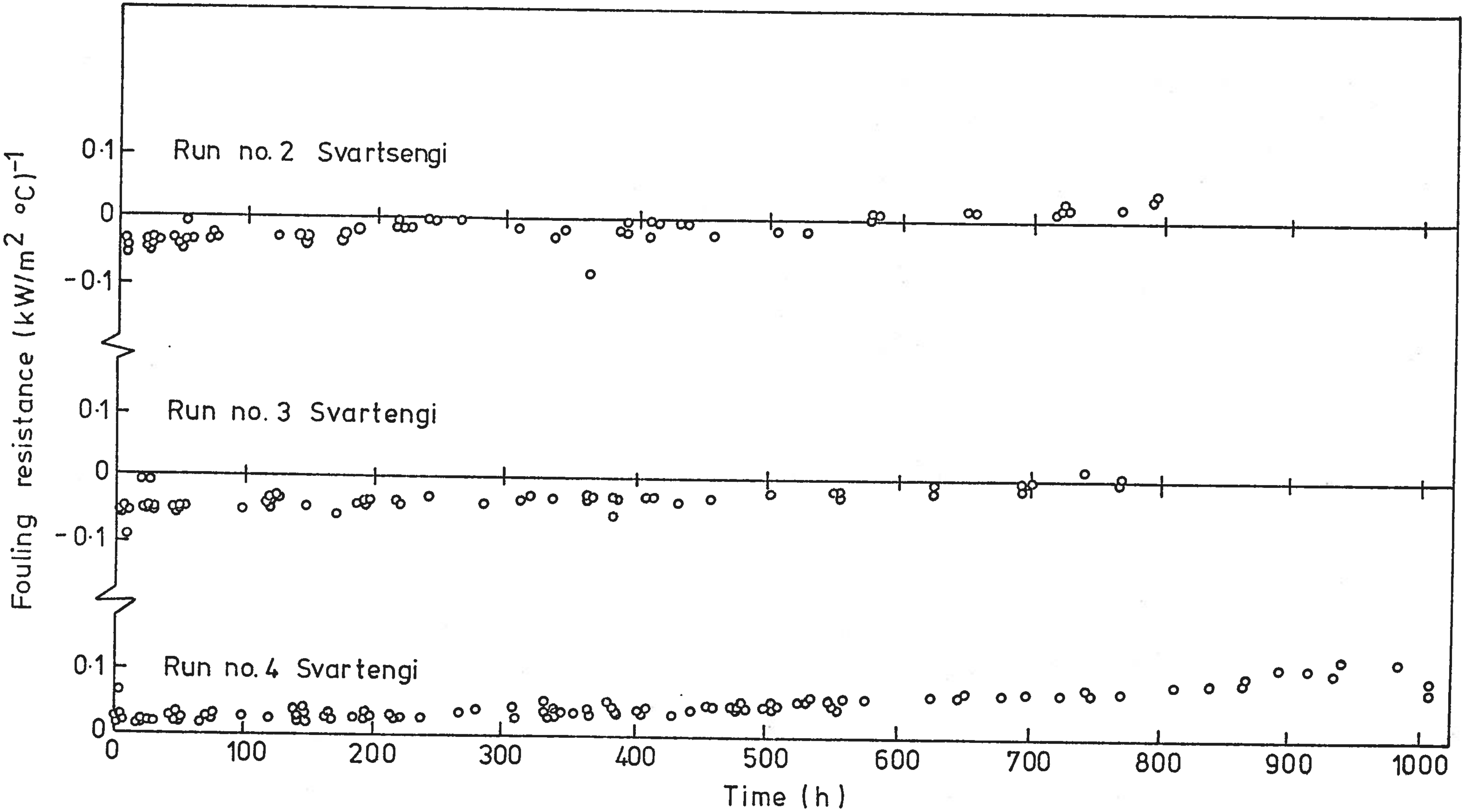

FIG. 1. FOULING RESISTANCE WITH TIME AT SVARTSENGI

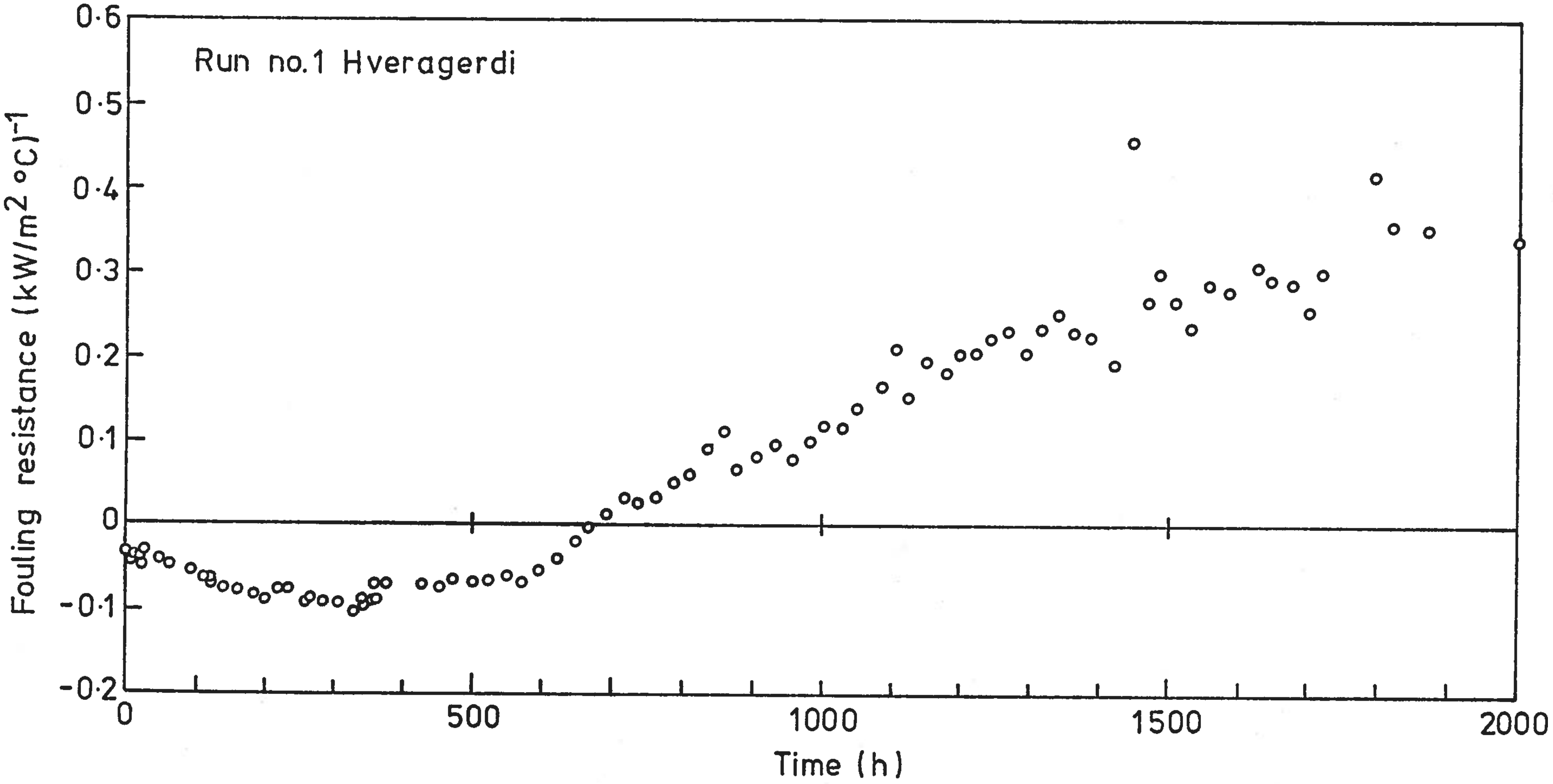

FIG. 2. FOULING RESISTANCE WITH TIME AT HVERAGERDI

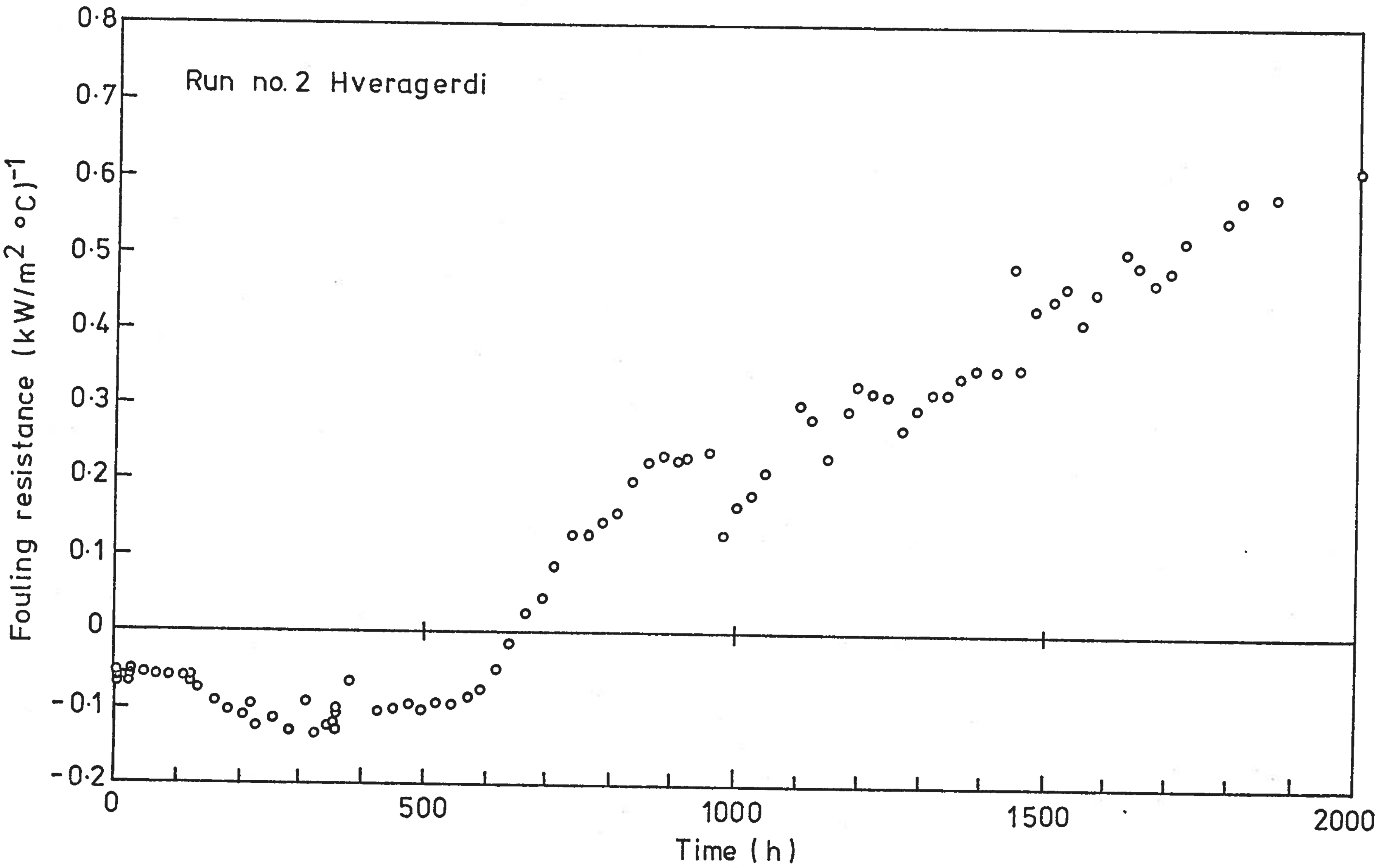

FIG. 3. FOULING RESISTANCE WITH TIME AT HVERAGERDI

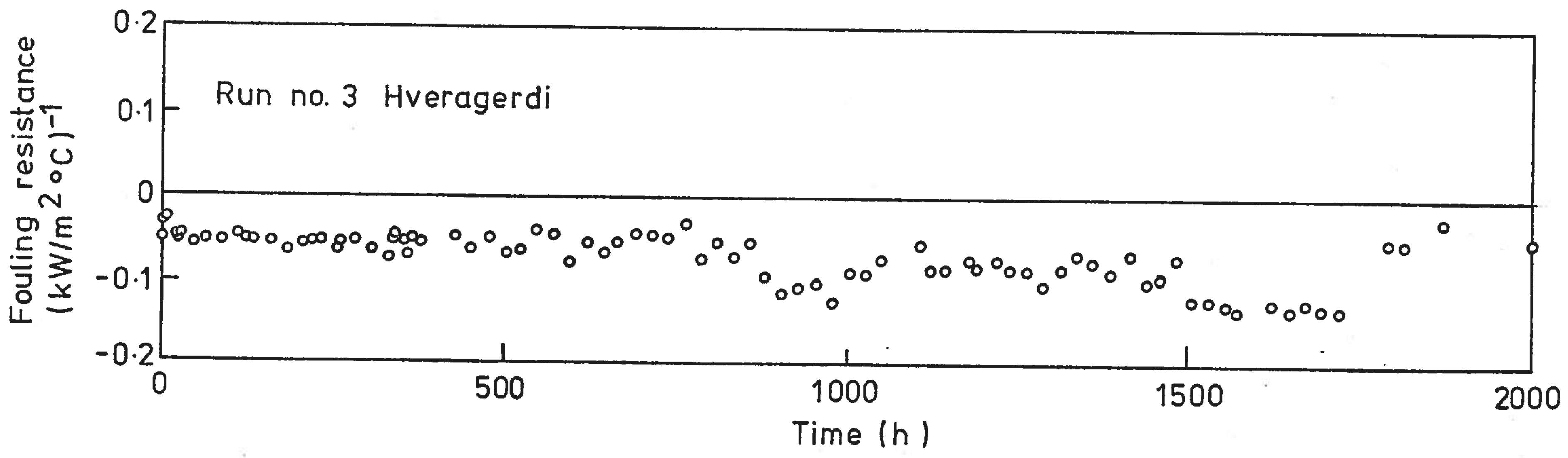

FIG. 4. FOULING RESISTANCE WITH TIME AT HVERAGERDI

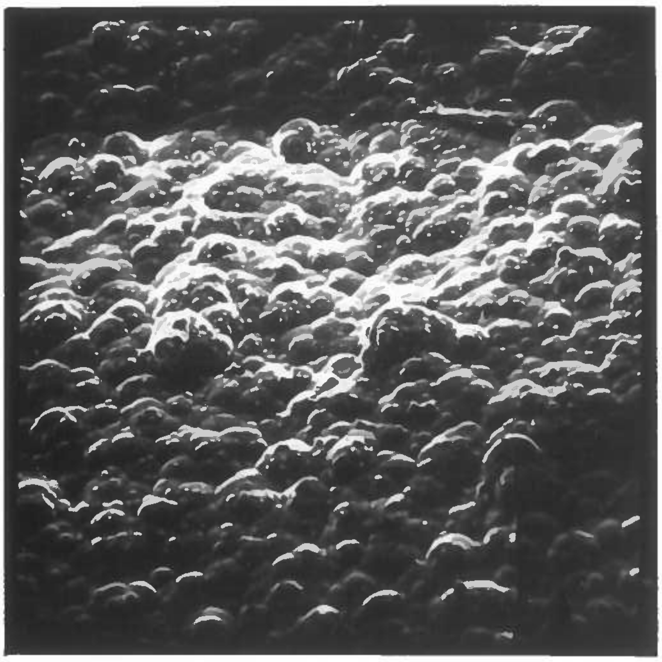

FIGURE 5a

Silica Deposit Tubular Exchanger Run No 2 Svartsengi 280x

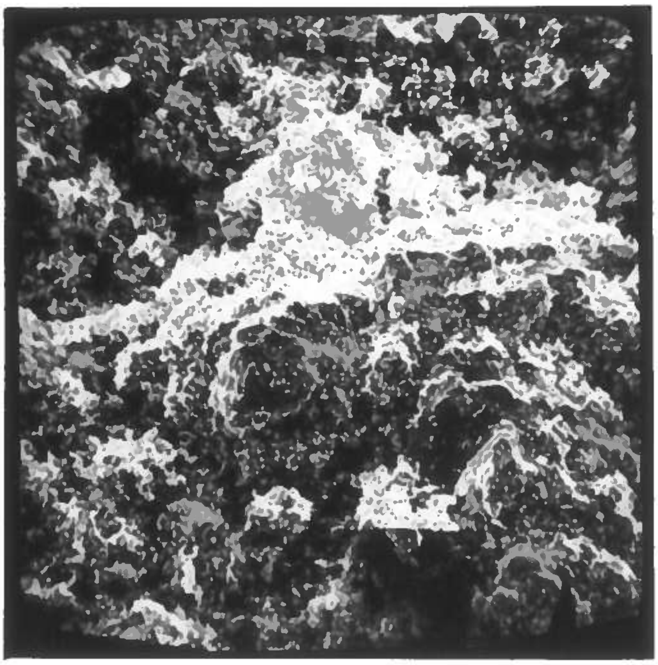

FIGURE 5b

Silica Deposit Plate Exchanger Run No 4 Svartsengi 280x

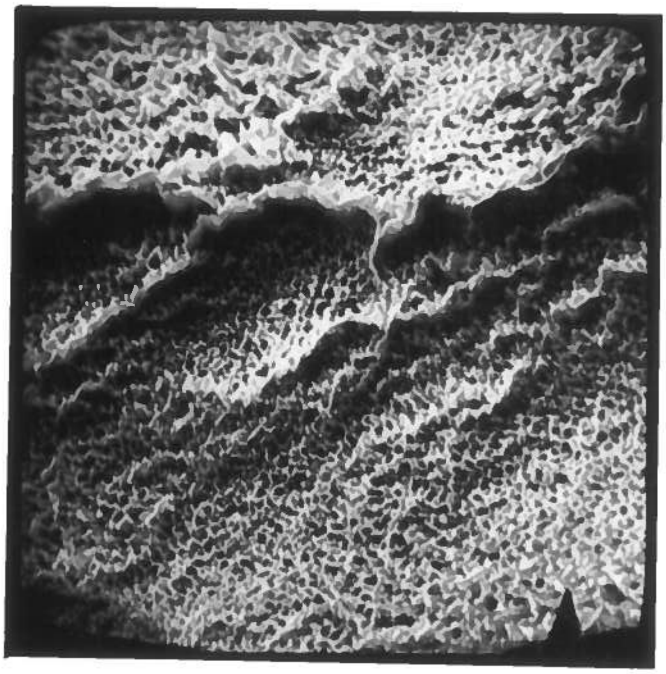

FIGURE 5c

Silica Deposit Tubular Exchanger Run No 1 Hveragerdi 280x

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EXPERIMENTAL RESULTS RUN 2 HVERAGERDI

DATE TIME THI THO TCI TCO WH WC

LMTD QH QC QRATIO QAVE HTCEXP

REH PRH NUH HTCH REC PRC NUC HTCC

HTCEMP HRATIO HOURS RF

DATE : Date
TIME : Time
THI : Temperature, hot water, inlet (°C)
THO : Temperature, hot water, outlet (°C)
TCI : Temperature, cold water, inlet (°C)
TCO : Temperature, cold water, outlet (°C)
WH : Flowrate, hot water (kg/s)
WC : Flowrate, cold water (kg/s)
LMTD : Log-mean temperature difference (°C)
QH : Rate of heat transfer, hot water (kW)
QC : Rate of heat transfer, cold water (kW)
QRATIO : QH/QC
QAVE : (QH + QC)/2
HTCEXP : Experimental overall heat transfer coefficient (kW/m^2 °C)
REH : Reynolds number, hot water
PRH : Prandtl number, hot water
NUH : Nusselt number, hot water
HTCH : Film heat transfer coefficient, hot side (kW/m^2 °C)
REC : Reynolds number, cold water
PRC : Prandtl number, cold water
NUC : Nusselt number, cold water
HTCC : Film heat transfer coefficient, cold water (kW/m^2 °C)
HTCEMP : Empirical overall heat transfer coefficient (kW/m^2 °C)
HRATIO : HTCEMP/HTCEXP
HOURS : Experimental time (h)
RF : Calculated fouling resistance $(kW/m^2\ {}^{\circ}C)^{-1}$

14.08 15.00 78.00 58.50 14.20 26.00 0.0861 0.1384
48.05 7.22 6.84 1.027 6.93 2.983
25776.0 2.64 114.40 7.3250 12023.0 6.94 94.53 7.2919
2.601 0.872 0.0 -.0492

14.08 15.50 78.90 59.00 13.20 26.50 0.0863 0.1375
49.03 7.19 7.66 0.938 7.42 3.131
26097.4 2.61 114.99 7.3690 11872.9 6.99 93.84 7.2350
2.597 0.829 0.50 -.0657

14.08 16.50 77.00 57.00 13.20 25.20 0.0774 0.1465
47.69 6.47 7.36 0.879 6.92 3.000
22769.7 2.69 104.54 6.6836 12449.8 7.11 98.16 7.5555
2.555 0.852 1.50 -.0580

15.08 10.50 76.80 56.60 13.00 25.00 0.0774 0.1500
47.58 6.54 7.54 0.867 7.04 3.059
22678.5 2.70 104.42 6.6735 12685.4 7.15 99.85 7.6823
2.573 0.841 19.50 -.0618

15.08 11.50 76.50 56.50 13.00 25.00 0.0771 0.1487
47.39 6.45 7.48 0.862 6.96 3.038
22515.4 2.71 103.97 6.6427 12577.9 7.15 99.18 7.6305
2.561 0.843 20.50 -.0613

15.08 12.50 76.20 56.40 13.00 25.00 0.0774 0.1500
47.19 6.41 7.54 0.850 6.98 3.056
22553.3 2.72 104.25 6.6591 12685.4 7.15 99.85 7.6823
2.571 0.841 21.50 -.0618

15.08 13.50 79.00 58.40 13.40 25.80 0.0760 0.1426
48.99 6.55 7.41 0.884 6.93 2.946
22889.2 2.62 103.78 6.6484 12244.1 7.03 96.44 7.4303
2.531 0.859 22.50 -.0556

16.08 15.00 76.00 58.00 13.00 25.00 0.1007 0.1467
47.94 7.58 7.38 1.028 7.48 3.227
29638.8 2.69 128.92 8.2421 12409.6 7.15 98.12 7.5493
2.754 0.853 48.00 -.0532

17.08 8.00 79.00 57.20 13.20 25.00 0.0725 0.1523
48.83 6.61 7.53 0.878 7.07 2.995

21668.3 2.64 99.76 6.3860 12915.6 7.13 101.18 7.7862
2.544 0.849 65.00 -.0592

18.08 8.00 80.20 58.00 13.30 25.20 0.0780 0.1505
49.67 7.24 7.50 0.965 7.37 3.069
23621.0 2.60 106.12 6.8018 12807.3 7.10 100.33 7.7241
2.598 0.847 89.00 -.0591

19.08 8.00 79.00 56.70 13.10 24.50 0.0732 0.1532
48.85 6.83 7.31 0.934 7.07 2.994
21799.2 2.65 100.40 6.4256 12888.7 7.19 101.35 7.7936
2.551 0.852 113.00 -.0580

19.08 15.00 78.00 55.80 13.00 24.00 0.0729 0.1488
48.18 6.77 6.86 0.987 6.81 2.923
21412.9 2.69 99.63 6.3685 12425.7 7.25 98.77 7.5902
2.513 0.869 120.00 -.0558

19.08 17.00 79.00 58.20 13.00 25.60 0.0862 0.1462
49.19 7.50 7.72 0.972 7.61 3.199
25930.7 2.62 114.68 7.3457 12458.4 7.09 98.10 7.5531
2.646 0.827 122.00 -.0653

20.08 8.00 79.50 57.90 13.00 26.00 0.0870 0.1528
49.07 7.86 8.32 0.944 8.09 3.409
26205.0 2.62 115.56 7.4033 13085.6 7.05 101.78 7.8402
2.699 0.792 137.00 -.0771

21.08 8.00 78.20 56.50 13.00 26.20 0.0881 0.1497
47.62 8.00 8.28 0.966 8.14 3.533
26050.4 2.67 116.07 7.4239 12848.4 7.03 100.20 7.7204
2.683 0.760 161.00 -.0896

22.08 8.00 77.00 55.00 13.00 26.50 0.0864 0.1464
46.12 7.95 8.28 0.960 8.11 3.638
25069.7 2.73 113.63 7.2555 12614.9 7.00 98.59 7.5987
2.642 0.726 185.00 -.1037

23.08 8.00 80.50 56.50 13.00 27.60 0.0824 0.1478
48.05 8.27 9.04 0.915 8.66 3.726
24758.9 2.63 110.61 7.0845 12910.9 6.90 99.81 7.7035
2.635 0.707 209.00 -.1111

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47.34    7.71    8.11   0.951    7.91   3.456
 25131.0  2.67  112.81     7.2149     12153.6  6.79    95.43      7.3578
2.598   0.752   217.00   -.0956

24.08    8.00   81.00   56.50   13.50   28.00   0.0826   0.1437
47.83    8.64    9.03   0.956    8.83   3.819
 24812.1  2.63  111.80     7.0966     12610.7  6.86    97.75      7.5478
2.612   0.684   233.00   -.1209

25.08    8.50   80.00   53.50   12.50   25.50   0.0755   0.1586
47.43    8.37    8.64   0.968    8.50   3.707
 22135.5  2.70  102.40     6.5443     13417.5  7.15   104.41      8.0327
2.603   0.702   257.50   -.1145

25.08   11.50   79.00   53.50   12.60   26.00   0.0762   0.1512
46.69    8.12    8.49   0.957    8.31   3.679
 22173.0  2.72  102.89     6.5715     12886.4  7.09   100.77      7.7587
2.569   0.698   262.50   -.1175

26.08    9.00   80.00   54.00   12.50   27.50   0.0796   0.1560
46.78    8.66    9.82   0.883    9.23   4.080
 23430.5  2.69  106.95     6.8373     13523.9  6.96   103.91      8.0136
2.645   0.648   282.00   -.1329

27.08    9.00   81.00   57.50   12.50   26.20   0.0722   0.1572
49.74    7.10    9.02   0.787    8.06   3.351
 21919.7  2.63   99.90     6.4041     13410.2  7.08   103.96      8.0049
2.577   0.769   306.00   -.0897

28.08    8.50   81.50   57.00   12.50   30.00   0.0762   0.1129
47.91    7.81    8.27   0.943    8.04   3.470
 23119.6  2.60  104.22     6.6813     10088.0  6.73    81.19      6.2803
2.344   0.676   329.50   -.1384

28.08   18.00   76.22   52.00   13.00   26.00   0.0727   0.1487
44.26    7.36    8.10   0.908    7.73   3.601
 20527.7  2.81   98.22     6.2566     12730.7  7.05    99.58      7.6707
2.507   0.696   339.00   -.1212

28.08   20.50   81.50   56.00   12.50   27.50   0.0778   0.1555
48.56    8.30    9.77   0.849    9.03   3.846
 23446.4  2.62  105.75     6.7749     13476.0  6.96   103.61      7.9910
2.633   0.685   341.50   -.1198


29.08    8.00   80.50   54.80   12.50   28.00   0.0795   0.1543
47.22    8.54   10.02   0.852    9.28   4.064
 23592.0  2.66  107.06     6.8499     13461.0  6.91   103.24      7.9668
2.640   0.650   353.00   -.1327

29.08   10.50   80.20   54.80   12.60   26.50   0.0782   0.1539
47.72    8.30    8.96   0.927    8.63   3.740
 23160.9  2.67  105.61     6.7558     13191.6  7.04   102.38      7.8873
2.615   0.699   355.50   -.1151

29.08   12.00   80.20   57.00   12.60   27.00   0.0384   0.1499
48.67    8.58    9.04   0.949    8.81   3.744
 26608.1  2.62  117.05     7.4978     12930.7  6.99   100.49      7.7462
2.697   0.720   357.00   -.1037

30.08    8.50   81.00   57.50   12.50   24.00   0.0867   0.1534
50.76    8.52    7.39   1.152    7.96   3.241
 26303.6  2.60  115.48     7.4030     12736.7  7.33   101.02      7.7578
2.686   0.829   377.50   -.0637

 1.09    8.00   81.00   57.50   12.80   27.50   0.0849   0.1484
48.97    8.34    9.13   0.913    8.74   3.690
 25762.6  2.60  113.59     7.2817     12907.6  6.93    99.96      7.7119
2.663   0.722   425.00   -.1045

 2.09    8.00   81.20   57.80   13.00   27.50   0.0850   0.1489
49.12    8.32    9.04   0.921    8.68   3.655
 25897.8  2.59  113.87     7.3020     12983.1  6.91   100.31      7.7411
2.670   0.731   449.00   -.1009

 3.09    8.00   83.50   59.00   13.20   27.50   0.0349   0.1454
50.73    8.70    8.71   0.999    8.71   3.549
 26477.9  2.52  114.57     7.3613     12712.6  6.89    98.54      7.6061
2.657   0.749   473.00   -.0946

 4.09    8.00   81.50   57.50   13.00   27.50   0.0849   0.1479
49.10    8.52    8.98   0.949    8.75   3.686
 25850.9  2.59  113.71     7.2915     12895.5  6.91    99.77      7.6996
2.662   0.722   497.00   -.1043

 5.09    8.00   80.50   57.50   13.00   27.00   0.0865   0.1502
48.86    8.32    8.81   0.945    8.56   3.624
 26161.1  2.61  115.18     7.3813     [illegible]  [illegible]  [illegible]  [illegible]
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6.09 8.00 79.50 57.50 13.00 27.00 0.0881 0.1476
48.39 8.10 8.66 0.936 8.38 3.591
26456.8 2.63 116.60 7.4681 12797.4 6.96 99.44 7.6694
2.681 0.749 545.00 -.0938

7.09 9.50 79.50 58.00 13.00 26.50 0.0875 0.1499
48.89 7.87 8.48 0.928 8.17 3.457
26380.7 2.62 116.14 7.4407 12916.8 7.00 100.46 7.7430
2.689 0.778 570.50 -.0826

8.09 9.00 81.00 58.50 12.50 25.50 0.0860 0.1539
50.60 8.10 8.38 0.966 8.24 3.367
26286.8 2.58 115.04 7.3790 13017.3 7.15 101.92 7.8417
2.696 0.801 594.00 -.0739

9.09 8.00 80.50 59.80 12.80 25.00 0.0830 0.1487
51.13 7.19 7.60 0.945 7.39 2.990
25501.3 2.56 112.00 7.1874 12546.7 7.17 99.09 7.6221
2.636 0.882 617.00 -.0449

10.09 8.00 80.50 60.50 12.80 24.00 0.0725 0.1485
51.98 6.06 6.97 0.870 6.52 2.593
22374.3 2.55 100.71 6.4652 12373.7 7.27 98.56 7.5715
2.525 0.974 641.00 -.0103

11.09 8.00 82.50 63.50 12.80 24.00 0.0735 0.1348
54.51 5.84 6.33 0.923 6.08 2.308
23453.0 2.46 102.86 6.6219 11233.2 7.27 91.26 7.0113
2.462 1.067 665.00 0.0271

12.09 8.00 81.50 63.00 13.00 23.00 0.0765 0.1454
54.14 5.93 6.09 0.973 6.01 2.295
24193.7 2.49 105.94 6.8150 11989.7 7.35 96.55 7.4101
2.552 1.112 689.00 0.0439

13.09 8.00 80.50 63.50 12.80 22.00 0.0730 0.1454
54.51 5.19 5.61 0.926 5.40 2.048
22986.9 2.50 101.89 6.5521 11812.3 7.47 96.06 7.3618
2.507 1.224 713.00 0.0894

14.09 8.00 81.00 64.50 13.00 21.50 0.0723 0.1457
55.40 4.99 5.19 0.962 5.09 1.899
22991.5 2.47 101.41 6.5268 11788.4 7.51 96.07 7.3598
2.503 1.318 737.00 0.1270

15.09 8.00 82.00 65.00 13.00 21.50 0.0720 0.1464
56.14 5.13 5.21 0.983 5.17 1.904
23156.0 2.44 101.49 6.5377 11847.4 7.51 96.45 7.3890
2.509 1.317 761.00 0.1265

16.09 8.00 78.00 62.50 12.80 20.50 0.0717 0.1502
53.51 4.65 4.85 0.960 4.75 1.835
22071.9 2.56 99.79 6.4043 11969.2 7.63 97.91 7.4893
2.564 1.364 785.00 0.1455

17.09 8.00 78.50 63.00 12.20 20.00 0.0703 0.1460
54.56 4.56 4.77 0.955 4.67 1.768
21782.3 2.54 98.42 6.3202 11460.8 7.75 95.24 7.2751
2.459 1.391 809.00 0.1589

18.09 8.00 79.00 64.50 12.50 20.00 0.0684 0.1494
55.43 4.15 4.70 0.884 4.42 1.651
21482.7 2.51 96.71 6.2172 11787.5 7.72 97.17 7.4254
2.466 1.494 833.00 0.2002

19.09 8.00 81.50 66.00 12.80 20.00 0.0668 0.1457
57.25 4.33 4.40 0.985 4.36 1.577
21530.3 2.44 95.63 6.1619 11538.9 7.69 95.37 7.2908
2.437 1.546 857.00 0.2240

20.09 8.00 77.50 63.00 12.50 19.00 0.0674 0.1485
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20740.8 2.56 94.97 6.0953 11559.9 7.83 96.23 7.3442
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21.09 8.00 78.50 64.00 12.50 19.50 0.0663 0.1484
55.17 4.02 4.36 0.923 4.19 1.570
20673.1 2.52 94.10 6.0466 11633.8 7.78 96.44 7.3649
2.430 1.548 905.00 0.2254

22.09 8.00 80.00 65.00 12.50 19.50 0.0655 0.1474
56.41 4.11 4.33 0.950 4.22 1.547
20771.1 2.48 93.69 6.0286 11555.7 7.78 95.93 7.3255
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23.09 8.00 79.50 64.50 12.70 19.50 0.0622 0.1492
55.80 3.96 4.25 0.918 4.08 1.511

24.09 8.00 79.00 58.00 12.00 19.00 0.0467 0.1518
52.69 4.10 4.45 0.921 4.28 1.679
14028.3 2.63 72.45 4.5124 11742.6 7.89 97.72 7.4532
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25.09 8.00 81.00 60.00 12.00 19.00 0.0450 0.1453
54.70 3.96 4.26 0.928 4.11 1.554
13903.1 2.55 68.99 4.4290 11238.0 7.89 94.37 7.1974
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26.09 8.00 79.00 59.50 12.00 18.50 0.0487 0.1521
53.74 3.97 4.14 0.958 4.06 1.561
14779.0 2.60 73.03 4.6813 11687.6 7.95 97.64 7.4423
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27.09 8.00 78.50 59.00 12.00 18.00 0.0462 0.1516
53.47 3.77 3.81 0.988 3.79 1.466
13922.0 2.62 69.87 4.4765 11572.5 8.00 97.16 7.4008
2.133 1.456 1049.00 0.2135

29.09 15.50 83.00 63.80 12.00 18.10 0.0508 0.1477
56.70 3.44 3.78 0.912 3.61 1.317
15985.8 2.50 76.38 4.9114 11295.3 7.99 95.25 7.2562
2.210 1.678 1104.50 0.3068

30.09 8.00 83.50 69.50 12.00 19.00 0.0735 0.1485
60.93 4.31 4.36 0.989 4.33 1.470
24548.5 2.34 104.32 6.7410 11484.7 7.89 96.01 7.3227
2.528 1.720 1121.00 0.2847

1.10 8.00 83.00 70.00 12.50 21.00 0.0738 0.1452
59.72 4.02 5.17 0.776 4.59 1.591
24646.6 2.34 104.65 6.7624 11601.7 7.61 95.40 7.2994
2.527 1.589 1145.00 0.2330

2.10 16.50 84.00 71.00 12.50 20.00 0.0749 0.1419
61.21 4.08 4.46 0.914 4.27 1.443
25361.4 2.31 106.39 6.8821 11197.2 7.72 93.28 7.1282
2.516 1.744 1177.50 0.2956

3.10 8.00 83.50 71.00 12.50 19.50 0.0751 0.1455
61.21 3.93 4.27 0.921 4.10 1.386
25347.2 2.32 106.51 6.8879 11402.7 7.78 94.91 7.2483
2.537 1.831 1193.00 0.3275

4.10 8.00 83.00 69.50 12.50 19.00 0.0743 0.1436
60.43 4.20 3.91 1.073 4.06 1.389
24744.4 2.35 105.14 6.7926 11182.2 7.83 93.72 7.1528
2.508 1.807 1217.00 0.3218

5.10 8.00 82.50 69.50 12.00 19.00 0.0710 0.1458
60.45 3.86 4.28 0.903 4.07 1.392
23567.0 2.36 101.30 6.5429 11275.2 7.89 94.62 7.2163
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6.10 8.00 81.50 68.50 12.00 20.00 0.0684 0.1452
58.96 3.72 4.87 0.764 4.30 1.506
22409.3 2.39 97.94 6.3191 11382.3 7.78 94.78 7.2380
2.454 1.629 1265.00 0.2562

7.10 8.00 81.50 68.00 12.00 19.00 0.0658 0.1485
59.19 3.72 4.36 0.853 4.04 1.410
21490.1 2.40 94.88 6.1202 11484.7 7.89 96.01 7.3227
2.435 1.727 1289.00 0.2984

8.10 8.00 82.50 69.50 12.00 19.00 0.0694 0.1458
60.45 3.78 4.28 0.883 4.03 1.377
23035.3 2.36 99.48 6.4253 11275.2 7.89 94.62 7.2163
2.466 1.790 1313.00 0.3205

9.10 8.00 83.50 71.00 12.50 20.00 0.0697 0.1426
60.97 3.65 4.48 0.814 4.07 1.379
23519.1 2.32 100.35 6.4900 11251.7 7.72 93.64 7.1558
2.466 1.788 1337.00 0.3195

10.10 8.00 82.50 70.50 12.50 19.50 0.0704 0.1479
60.47 3.54 4.34 0.815 3.94 1.347
23530.6 2.34 100.86 6.5179 11594.6 7.78 96.18 7.3451
2.499 1.855 1361.00 0.3421

11.10 8.00 83.50 71.00 12.50 19.50 0.0669 0.1453
61.21 3.50 4.26 0.822 3.88 1.311
22568.1 2.32 97.11 6.2805 11383.8 7.78 94.79 7.2388
2.448 1.866 1385.00 0.3540

12.10 16.00 81.00 68.00 12.50 18.50 0.0712 0.1465
58.93 3.88 3.68 1.052 3.78 1.326
23190.4 2.41 100.97 6.5108 11333.1 7.89 95.00 7.2458
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13.10	10.00	72.00	65.00	12.50	18.50	0.0680	0.1477	
53.[illegible]	1.99	3.72	0.536	2.85	1.113			
20418.9	2.63	94.90	6.0781		11428.3	7.89	95.64	7.2941
2.425	2.173	1443.00	0.4860					
14.10	8.00	75.00	63.50	12.50	18.50	0.0616	0.1463	
53.70	2.96	3.68	0.806	3.32	1.279			
18703.5	2.60	88.06	5.6451		11314.2	7.89	94.88	7.2362
2.345	1.833	1457.00	0.3554					
15.10	8.00	78.50	66.50	12.50	18.00	0.0611	0.1465	
57.19	3.07	3.38	0.959	3.22	1.166			
19386.2	2.49	88.69	5.7068		11260.5	7.95	94.79	7.2252
2.354	2.019	1481.00	0.4330					
16.10	8.00	78.00	66.50	12.50	18.00	0.0611	0.1488	
56.95	2.94	3.43	0.858	3.19	1.157			
19321.8	2.49	88.60	5.6994		11432.0	7.95	95.94	7.3126
2.365	2.044	1505.00	0.4415					
17.10	8.00	77.00	66.00	12.50	18.00	0.0584	0.1480	
56.21	2.69	3.41	0.788	3.05	1.123			
18291.6	2.52	85.24	5.4785		11374.3	7.95	95.55	7.2832
2.322	2.068	1529.00	0.4600					
18.10	8.00	78.00	66.50	12.50	18.50	0.0579	0.1487	
56.71	2.79	3.74	0.745	3.26	1.190			
18309.6	2.49	84.89	5.4607		11505.6	7.89	96.15	7.3333
2.325	1.953	1553.00	0.4100					
19.10	8.00	81.00	68.00	12.50	18.00	0.0556	0.1478	
59.17	3.03	3.41	0.888	3.22	1.124			
18103.5	2.41	82.92	5.3473		11355.1	7.95	95.43	7.2735
2.297	2.043	1577.00	0.4543					
21.10	8.00	81.50	68.00	12.50	17.50	0.0533	0.1461	
59.65	3.01	3.06	0.984	3.04	1.053			
17410.0	2.40	80.26	5.1770		11150.9	8.00	94.33	7.1856
2.253	2.141	1625.00	0.5061					
22.10	8.00	83.50	72.00	12.50	18.00	0.0700	0.1485	
62.45	3.37	3.42	0.985	3.40	1.125			
23770.6	2.31	100.89	6.5282		11412.7	7.95	95.81	7.3028
2.494	2.217	1649.00	0.4879					
23.10	8.00	71.50	63.00	12.00	17.00	0.0783	0.1480	
52.73	2.78	3.10	0.897	2.94	1.154			
23109.5	2.68	105.60	6.7533		11154.1	8.12	94.91	7.2202
2.514	2.178	1673.00	0.4687					
24.10	8.00	80.00	69.50	12.00	17.50	0.0727	0.1456	
59.97	3.20	3.36	0.952	3.28	1.130			
23756.9	2.40	102.76	6.6282		11040.9	8.06	93.87	7.1455
2.484	2.199	1697.00	0.4825					
25.10	8.00	81.50	71.50	12.00	17.50	0.0754	0.1437	
61.72	3.16	3.31	0.953	3.23	1.084			
25186.5	2.34	106.47	6.8799		10896.6	8.06	92.89	7.0711
2.507	2.313	1721.00	0.5238					
28.10	8.00	79.50	67.00	12.00	16.50	0.0564	0.1486	
58.91	2.95	2.80	1.053	2.88	1.010			
18075.5	2.45	83.49	5.3763		11118.9	8.18	94.95	7.2186
2.295	2.272	1793.[illegible]	0.5542					
29.10	8.00	79.50	67.50	12.00	16.50	0.0572	0.1473	
59.17	2.87	2.78	1.033	2.83	0.987			
18370.6	2.44	84.43	5.4387		11025.8	8.18	94.32	7.1705
2.299	2.329	1817.00	0.5779					
31.10	11.50	80.00	69.00	12.00	16.50	0.0654	0.1514	
6[illegible].19	3.01	2.86	1.054	2.93	1.008			
21294.3	2.41	94.35	6.0839		11329.4	8.18	96.38	7.3271
2.430	2.411	1868.51	0.5807					
7.11	9.50	79.00	69.00	11.50	16.00	0.0686	0.1503	
60.21	2.87	2.84	1.012	2.85	0.980			
22183.0	2.43	97.77	6.3[illegible]16		11103.8	8.30	95.41	7.2442
2.452	2.502	2034.50	0.6124					
22605.0	12021.4	2.505	0.141					