[redacted]

CONF-8005157--1

Doc Ch · 700 301

MASTER

Effect of Microfouling on Heat-Transfer Efficiency

Brenda Little

and

Leslie Ralph Berger

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

ABSTRACT

Field experiments, performed at Keahole Point, Hawaii and in the Gulf of Mexico, were designed to determine the relationship between decreased heat transfer efficiency and the accumulation of corrosion and/or biofouling films on heat exchanger surfaces. The sample tubes were maintained under conditions simulating those of an Ocean Thermal Energy Conversion (OTEC) system and data from the two sites have been compared. Seawater flowed through 2.54 (internal diameter) metal tubes at approximately 1.8m sec^{-1}. Four types of tubes were used: 5052 Aluminum (Al), Grade 2 titanium (Ti), 90-10 copper-nickel (Cu-Ni) and Allegheny-Ludlum 6X stainless steel (SS).

All surfaces were colonized by microorganisms, though colonization of the Cu-Ni surface was initially retarded. Total film weight was greatest for the Al and Cu-Ni surfaces which were characterized by corrosion as well as microbial fouling. The total organic carbon:total nitrogen ratios of the fouling films from Ti, Al, SS and Cu-Ni, 4.2, 4.0, 4.8 and 7.9 respectively, remained constant throughout the experiment. The degradation of heat transfer efficiency due to the formation of fouling layers on Ti and SS is neither linear nor a simple exponential function. A microfouling model is proposed for corrosion-resistant surfaces that is consistent with field observations.

INTRODUCTION

Ocean Thermal Energy Conversion (OTEC) is a concept which employs the difference in temperature between warm surface waters and cold deep waters to generate energy. In marine environments, the temperature differential is only about 20°C, thus, the efficiency of such a system is quite low. Operation of an OTEC system requires the maintenance of efficient heat exchangers. Insulating material in the form of fouling layers less than 100 μm thick can render such a system inoperative. Several processes can contribute to the formation of such layers: formation of corrosion products, deposition of inorganic salts, adsorption of dissolved organic material, colonization by microorganisms and the accumulation of their metabolic products, and the adhesion of detritus. The contribution of the various factors is dependent on the type of metal used in the heat exchanger, flow conditions, geographical location of exposure and environmental parameters. OTEC experiments were conducted in the Gulf of Mexico (GOM) and Hawaii (HI) to collect fouling data and to correlate those data with heat transfer efficiency.

METHODS AND MATERIALS

Details of the construction, operation, sample collection, and analytical procedures of the GOM and HI experiments have been previously presented (Liebert, et al., 1979; Little, et al., 1979). The HI experiments took place 300 meters off the coast of Keahole Point, HI; the GOM experiment 257 km due west of Tampa, FL. The alloys used for the heat exchangers were 5052 aluminum (Al), Grade 2 titanium (Ti), Allegheny-Ludlum 6X stainless steel (SS) and CDA 706 copper-nickel (Cu-Ni). Except for occasional malfunctions, seawater from the upper mixed layer flowed through 2.5 cm (i.d) tubes continuously at a nominal flow rate of 2 meters per second.

The instruments used for the measurement of heat transfer resistance (R_f) were designed at Carnegie-Mellon University (Fetkovich, 1977) and modified by Argonne National Laboratory. R_f is expressed as hr. ft.^{2} °F/BTU units. To convert to international R_f units (°C $m^2 w^{-1}$) multiply R_f values by 0.176. R_f is defined as the difference between 1/h where h is the measured heat transfer coefficient at any given time and the initial value of 1/h. Reference 2 discusses the corrections, based on water temperature and flow rate, used to calculate the heat transfer coefficient and fouling factor.

A modified M.A.N. brush (Nübel, 1977) was passed through the tubes of the HI experiment during flow to clean the fouling layers from the tube surfaces. Cleaned tubes were allowed to refoul. Sections from the flow systems of the two experiments were removed periodically and the following constituents and properties of the fouling layers quantified: total organic carbon, total nitrogen, dry film weight, wet film thickness and surface topography.

RESULTS AND DISCUSSION

Increased heat transfer resistance (R_f) as a function of time and alloy for both exposure sites is given in Figure 1 (a-d). There was a briefer lag period before increases in R_f could be measured for all surfaces exposed at the HI site as compared to the lag period experienced by the surfaces exposed in the GOM. There was no apparent lag period for the Cu-Ni surfaces at either site. Titanium surfaces consistently exhibited the longest lag period before there was measurable loss of heat transfer efficiency due to fouling.

Heat transfer resistance, total organic carbon (TOC) and total nitrogen (TN) are plott against exposure time for all alloys in Figure 2 (a-d). The scales of the ordinate were chosen such that the TOC and TN data for the titanium tube would superimpose on that of R_f. Ti and SS have similar chemical properties; neither corrodes vigorously in seawater (LaQue, 1979), nor is either toxic to microorganisms (Marszalek, 1979). One would therefore expect the two materials to exhibit nearly identical fouling and loss of heat transfer efficiency. The results shown in Figure 2 indicate that differences did exist.

One macroscopic difference was the topography of the two surfaces as received from the manufacturer. The inner surface of the SS tubes was marked with deep extrusion lines; these were absent in the titanium tubes (Figure 3a and b). It is unlikely that the nature of the microflora on the two metal surfaces is responsible for the differences observed in the R_f data. Differences were not detected in SEM micrographs of the two fouled surfaces. The biofilm on the stainless steel surface did obscure the surface roughness after 78 days (Figure 4).

Wet film thickness measurements were comparable for the period of investigation (Little, et al., 1979). TN:TOC ratios (Figure 5) and dry film weight:TOC ratios (Figure 6) in the fouling layers from the Ti and SS surfaces are very similar. The ratio of TOC to dry film weight was approximately 1:8 for both Ti and SS (Table 1) indicating that substantial amounts of inorganic materials are present in the fouling films. As stated previously, neither of those materials corrodes appreciably in seawater. The mucopolysaccharide secretions and microorganisms do chelate substantial amounts of inorganic salts from seawater (Siegel, 1971).

One explanation for the differing heat transfer responses observed for the two metals may be related to the surface roughness observed for the stainless steel. Water may become entrapped in the grooves of the stainless steel surface as the overlying biofilm develops, providing greater insulating effects. Thus, films with identical TOC, TN and wet film thickness would exhibit differing heat transfer responses.

Plots of R_f vs. dry film weight (Figure 7) and R_f vs. total organic carbon (Figure 8) for SS, Ti and Al indicate a linear relationship between the two. There also appears to be a linear relationship between R_f and TOC for SS and Ti. Such a correlation is not apparent for Al and Cu-Ni data. It appears (Figure 1) that for approximately the first 20 days the R_f of the Al surface is independent of both TOC and TN. It is during this period that the corrosion layer increases rapidly (Little & Lavoie, 1979). After about three weeks, the increase in R_f can be partially ascribed to TOC, and hence, biofilm formation. Corrosion of the Al surface during the first three weeks does adversely effect heat transfer efficiency.

The dry film weight of the Cu-Ni is an order of magnitude greater than that for the other metal surfaces (Figure 7). The increase in R_f with time for the Cu-Ni surface is largely due to the formation of a corrosion film. No correlation can be made between R_f and TOC or TN (Figure 9d). TOC:TN ratios for the Cu-Ni is substantially greater (Table 2) than that for the other materials (Figure 9 a-b). This is consistent with the hypothesis that microorganisms colonizing copper and other toxic metals secrete polymeric materials which chelate metal salts (Marszalek, 1979). Compounds such as polyuronic acid found in such secretions in the primary layer will raise the TOC:TN ratio for the entire film. Figure 10 is a micrograph of the colonized Cu-Ni heat exchanger surface showing both rod- and filamentous-type organisms.

CONCLUSIONS

There were no large changes in the TOC:TN ratios of the fouling films in each of the tube types during the experimental period. The ratios for Ti, SS, and Al were essentially the same (4.2, 4.8 and 4.0 respectively) while that of Cu-Ni was 7.9.

Increases in heat transfer resistance (R_f) for Ti and SS surfaces were related to the TOC and TN in the fouling films. However, the impacts of equivalent films were different on the two surfaces. A film covering the roughened SS surface may trap a film of water and provide a greater insulating effect than that observed on the smooth Ti surface. R_f was proportional to TOC and TN for Al surfaces only after prolonged exposure (>3 weeks). The formation of a corrosion film appeared to inhibit heat transfer efficiency during the first 3 weeks. Corrosion appeared to be responsible for increased R_f in the Cu-Ni tubes. The Cu-Ni was colonized by microorganisms, but their contribution to total dry film weight was small. The large film weights on all tubes, including the corrosion-resistant Ti and SS, suggested that the fouling films contain substantial amounts of inorganics that may effect R_f.

Cleaning with a M.A.N. brush removes most, but not all of the biomass in the fouling films. The first and second cleanings of the Al tubes reduced R_f to zero. Subsequent cleaning after 100 days appeared less effective. The rate of fouling increased after cleaning.

A model is proposed for the kinetics of biofouling on corrosion-resistant tubes such as Ti and SS maintained under the OTEC conditions described.

Sea water flowed through tubes (ID 2.5cm) at approximately 2 meters per second. Heat transfer resistance (R_f) was measured periodically and samples of the pipe were removed for analysis of the biofouling layer. Biofouling was assumed to be the cause of the increase in R_f for the corrosion-resistant metals. The rate of refouling after cleaning on such tubes is also considered in the model. The model is limited to early fouling in open ocean waters in which flow rates and water quality are assumed to remain constant during the experiment.

Description of the Biofouling Model

1. The rate of primary colonization, dC/dt depends on available uncolonized space, A', and the density of colonization per unit of space, a'. Since experimental data for A' and a' are lacking in the current studies only their product, A, ($A = A' \cdot a'$) is considered. The rate is also dependent on a variety of physical and chemical factors characteristic of the particular system. These factors are lumped together in a constant, K

$$dC/dt = (A - C)\,K \qquad (1a)$$

rearranging:

$$dC/(A - C) = K\,dt \qquad (1b)$$

Integrating (1b) between t=0 and ∞, (equation form: $dy = dx/(a + bx)$) gives:

$$C = A\,(1 - \exp -Kt) \qquad (2a)$$

or

$$C = A - A\,(\exp -Kt) \qquad (2b)$$

2. The growth of the primary colonizers (and/or production of metabolic products), S, is proportional to their number, the time, and a growth (or slime-production) constant, K_1. In the simplest form,

$$S = C \cdot K_1 \cdot t \qquad (3)$$

3. Secondary microbial colonization, i.e., biofouling by other organisms, N, depends upon time, S, and an adhesion constant, K_2: K_2 also includes a concentration factor, i.e., number of cells/volume of water.

$$N = S \cdot K_2 \cdot t \qquad (4)$$

4. Finally, total biomass, B, of the biofouled layer is

$$B = C + S + N \qquad (5)$$

5. Substitution of equations 1, 2, 3, 4, into 5 gives

$$B = A(\,(1 - e^{-Kt})\,(1 + K_1t + K_1K_2t^2)\,) \qquad (6)$$

It becomes evident that A is also a "scaling factor" dependent on the units used. When $K_2 >>> K_1$, the equation becomes largely dependent on the final term especially when t is not small and when K is small compared to K_1 and K_2.

1. The model ignores the various reactions which occur during the first minutes or hours following initiation of the flow of water. The first event considered in the model is the attachment (colonization) of those bacteria which have very high adhesive affinity for the tube surface. Colonization is random as the organisms come into contact with the surface from the seawater. Their rate of adhesion on the tube, however, depends on many factors:

   a. their numbers per unit volume of water
   b. their kind (i.e., their degree of "stickiness")
   c. the flow rate of the water and the hydrodynamic properties of flow
   d. the smoothness of the tube surface
   e. other factors such as temperature, organic content of the water, etc.
   f. the limited area for colonization

2. The initial colonizers are responsible for making the tube "sticky" for other groups of fouling bacteria. Growth of the primary colonizers, if it occurs, and slime production are assumed to be in direct proportion to cell number and time; nutrient concentration limits growth and metabolic product formation.

3. Other bacteria, secondary colonizers, adhere randomly to the surface at a rate proportional to their numbers and affinities as well as to the amount of

growth or slime already adhering to the tube surface. In the time frame considered no limitation of colonizing space is assumed for the secondary colonizers.

4. During the cleaning of the tubes it is assumed that the primary colonizers, their progeny and/or their macromolecular products are not removed. In contrast most or all of the secondary colonizers are assumed removed. Recolonization then occurs at a rate dependent on the amounts of adhering materials still on the pipe.

Analysis of Biofouling Model

Figure 9a shows three superimposed theoretical curves drawn over the R_f, total organic carbon and total nitrogen data from Ti in the HI experiment. The constants used in the model equation are given in Table 3. Since the magnitude and units of the 3 data sets are different, the constant A is scaled to give comparable numerical values for the Ti data. These same values of A are used for the SS data. The same values K and K_1 are used to generate all of the Ti curves. K_2 is chosen to make each curve fit the experimental data. For all Ti curves, K_2 varies little. Figure 11 shows a curve constructed through the data obtained in the Gulf of Mexico. Note from Table 3 that K_2 is only slightly lower than in the HI curves.

A larger value of K for SS (0.06) is required compared to that for Ti (0.01). This may result from the rougher surface of the SS or other factors which permitted the SS surface to be colonized more rapidly than that of Ti. Curves 3 through 10 in Figure 9b for SS mimic the increase in the fouling parameters after cleaning of the tube. Except for curves 1, 3 and 6, (Figure 9b) values of K_2 are relatively constant for each parameter. No explanation is offered for this apparent temporary increase in "secondary colonization" in curves 1, 3 and 6. Similar anomalies were not observed on any other tube or parameter measured.

For both the Ti and SS systems, the "secondary colonization" term is set back to a time value equivalent to the start of the experiment (zero to 3.5 days).

This supports the premise made in deriving the model. It further indicates that the model may be used to predict fouling rates after repeated cleaning of metal surfaces. The gradual rise in the starting value of R_f following repeated cleaning can be attributed to the combined C and S terms of the model: these are small numerically and unaffected by cleaning. They continue to increase with time.

The model curves generated for Ti and SS for GOM data, Figure 11, only fit in the early part of the experiment. It appears that the next stage of fouling, that which limits further rapid increase in R_f, was reached earlier than in the HI experiment. The model does not apply to this stage.

A single value of K_1 was used to generate all curves presented in Figures 9 (a-b) and 11. This value, 0.03, is arbitrary. The magnitude of K_2 is inversely related to K_1. An independent measurement of either "primary colonizers", C, and their products, S, or of "secondary colonizers", N, would permit assigning absolute values to K_1 and K_2.

The lower values given for K_2 in the organic carbon and nitrogen curves on SS compared to the R_f curves may not be due to differences in the rates of secondary colonization, but to different colonizing densities on Ti and SS surfaces. These should be distinguished in the constant A rather than in K_2.

The precision of the field data makes a more detailed analysis of the model impractical. It is evident that the fouling layer does not form in an exponential manner. This could occur under conditions in which nutrient levels are higher than those found in the present experiment. The model proposed by Bryers, et al. (1979), for biofouling was derived for a system exposed to light and in which nutrients were added. The present model does not include a term to limit the increase in the fouling rate.

REFERENCES

1. Bryers, J. D., W. G. Characklis, N. Zelver, and M. G. Nimmons. Microbial Film Development and Associated Energy Losses. Proceedings of the Sixth Ocean Thermal Energy Conference, Washington, D.C., June 19-22, 1979.
2. Fetkovich, J. G., G. N. Granneman, L. M. Mahalingham and D. L. Meier. Degradation of heat transfer rates due to biofouling and corrosion at Keahole Point, Hawaii. Proceedings of the Fourth OTEC Biofouling and Corrosion Symposium, Seattle, WA, October 10-12, 1977.
3. LaQue, F. L. Qualifications of stainless steel for OTEC heat exchanger tubing. ANL/OTEC report prepared for the U.S. Department of Energy Division of Central Solar Technology under contract W-31-109. January 1979.
4. Liebert, B. E., L. R. Berger, H. J. White, J. M. Moore, W. M. McCoy, J. A. Berger, and J. Larsen-Basse. The effects of biofouling and corrosion on heat transfer measurements. Proceedings of the Sixth Ocean Thermal Energy Conversion Conference, Washington, D.C., June 19-22, 1979.
5. Little, B. J. and D. M. Lavoie. Gulf of Mexico ocean thermal energy conversion (OTEC) biofouling and corrosion experiment. Proceedings of the OTEC Biofouling, Corrosion, and Materials Workshop, Rosslyn, VA, January 8-10, 1979.
6. Little, B., J. Morse, G. Loeb, and F. Spiehler. A biofouling and corrosion study of ocean thermal energy conversion (OTEC) heat exchanger candidate materials. Proceedings of the Sixth Ocean Thermal Energy Conversion Conference, Washington, D.C., June 19-22, 1979.
7. Marszalek, D. S., S. M. Gerchakov, L. R. Udey. Influence of substrate composition on marine microfouling. Applied and Environmental Microbiology, November 1979.
8. Nubel, E. D. Automatic tube cleaning system - brush and cage principle. Proceedings of the Fourth Ocean Thermal Energy Conversion Conference, New Orleans, LA, March 22-24, 1977.

9. Siegel, A. Metal-organic interactions in the marine environment. In Faust, S. D. and J. V. Hunter (eds.) Organic compounds in aquatic environments. Dekker, N. Y., 1971.

TABLE 1

RATIOS OF TOTAL ORGANIC CARBON TO R_f AND DRY FILM WEIGHT FROM STAINLESS STEEL & TITANIUM TUBES

SITE	HAWAII		GULF OF MEXICO	
	Ti	SS	Ti	SS
Organic C ($\mu g\ cm^{-2}$)	25.2	13.1	4.6	4.7
Film Dry Weight ($mg\ cm^{-2}$)	3.1	1.8	-	-
$R_f \times 10^4$ ($^\circ F\ ft^2 min\ BTU^{-1}$)	1.6	2.3	0.50	0.93
Ratio C/R_f	15.8	5.7	9.2	5.1
Ratio C/Dry Weight	8.1	7.3	-	-

Data for Gulf of Mexico are taken at 48 days; those for Hawaii are the arithmetic mean taken before the first cleaning.

TABLE 2

TOTAL ORGANIC CARBON TO TOTAL NITROGEN RATIOS IN FILMS ON VARIOUS TUBE TYPES

(HI Data)

Tube Type	TOC/TN Ratio*
Ti	4.2 ± 0.9
SS	4.8 ± 0.7
Al	4.0 ± 0.8
Cu-Ni	7.9 ± 0.8

*

1. Zero-values substracted for all but Al.
2. Average of 2 values for most times.
3. Values taken 1 day after cleaning or removal.
4. Wildly abberant values deleted.
5. Each ratio based on 12 or more values.

TABLE 3

BIOFOULING MODEL:

CONSTANTS GIVING GOOD FITTING CURVES THROUGH PLOTS OF THE EXPERIMENTAL DATA FOR FOULING BEFORE AND REFOULING OF TUBES AFTER CLEANING

SITE	TUBE TYPE	MEASURED PARAMETER	FOLLOWING CLEANING #	MODEL CONSTANTS*				DAY SERIES BEGUN	K2 PUSHED BACK TO ____ DAY	SEE FIG. #	CURVE #
				A	K	K1	K2				
GULF MEXICO	Ti	R_f	0	.00505	.01	.03	5.0	0	--	10	
HAWAII	Ti	R_f	0	.00505	.01	.03	6.5	0	--	9	1
HAWAII	Ti	R_f	1	.00505	.01	.03	6.5	94	0	9	2
HAWAII	Ti	Org. C	0	.06313	.01	.03	7.5	0	--	9	1
HAWAII	Ti	Org. C	1	.06313	.01	.03	6.5	94	0	9	2
HAWAII	Ti	N	0	.01683	.01	.03	6.5	0	--	9	1
HAWAII	Ti	N	1	.01683	.01	.03	6.0	94	0	9	2
GULF MEXICO	SS	R_f	0	.00505	.06	.03	5.5	0	--	10	
HAWAII	SS	R_f	0	.00505	.06	.03	6.0	0		9	1
HAWAII	SS	R_f	1	.00505	.06	.03	11.0	59	1	9	3
HAWAII	SS	R_f	2	.00505	.06	.03	17.0	94	0	9	6
HAWAII	SS	R_f	3	.00505	.06	.03	6.0	249	2	9	8
HAWAII	SS	R_f	4	.00505	.06	.03	7.5	263	3	9	9
HAWAII	SS	R_f	5	.00505	.06	.03	7.0	277	3.5	9	10
HAWAII	SS	Org. C	0	.06313	.06	.03	4.5	0	--	9	2
HAWAII	SS	Org. C	1	.06313	.06	.03	5.5	59	1	9	4
HAWAII	SS	Org. C	2	.06313	.06	.03	4.5	94	0	9	7
HAWAII	SS	N	0	.01683	.06	.03	4.0	0	--	9	2
HAWAII	SS	N	1	.01683	.06	.03	4.5	59	1	9	5
HAWAII	SS	N	2	.01683	.06	.03	4.0	94	0	9	7

*See text for explanation of symbols.

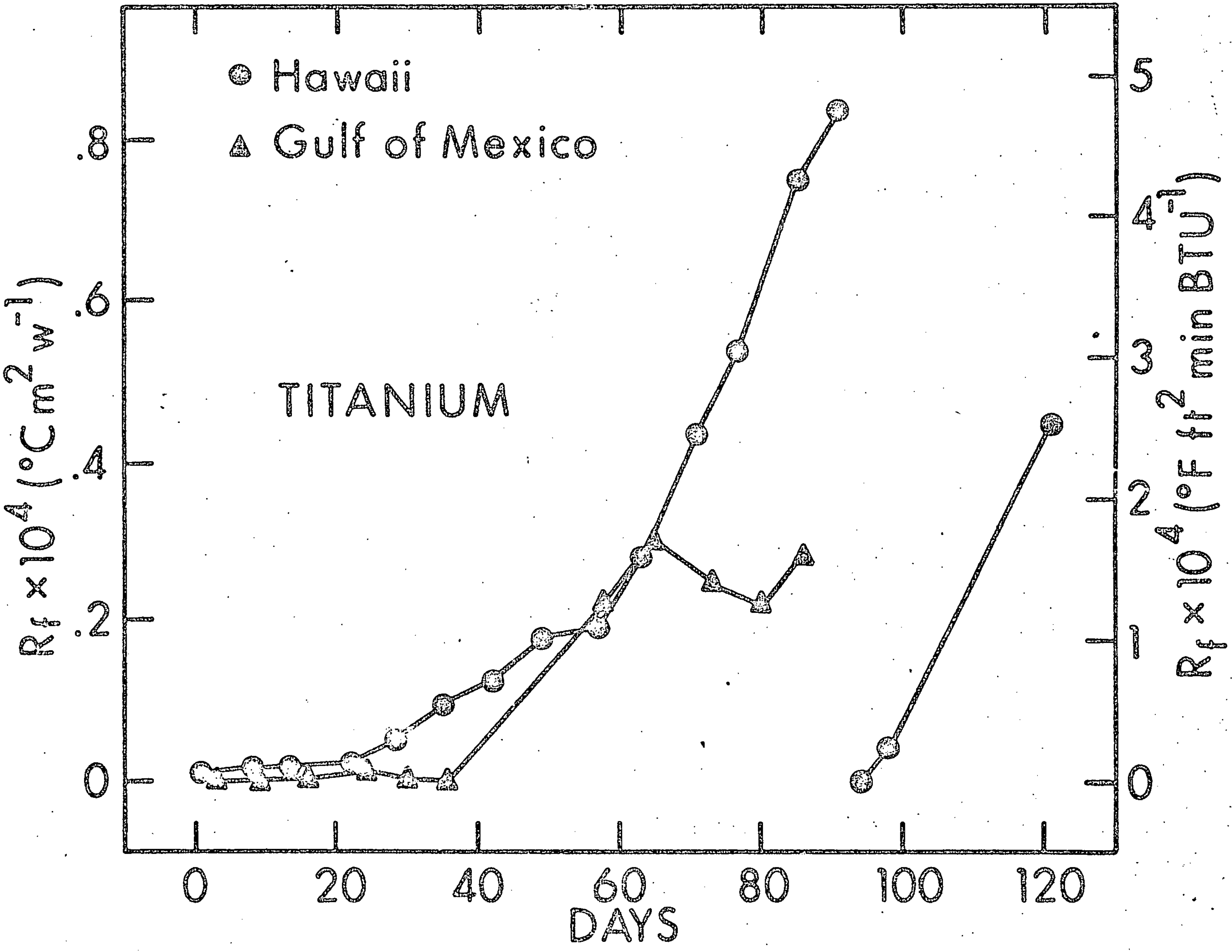

Figure 1a. R_f vs. time for data from the two experimental sites for Ti.

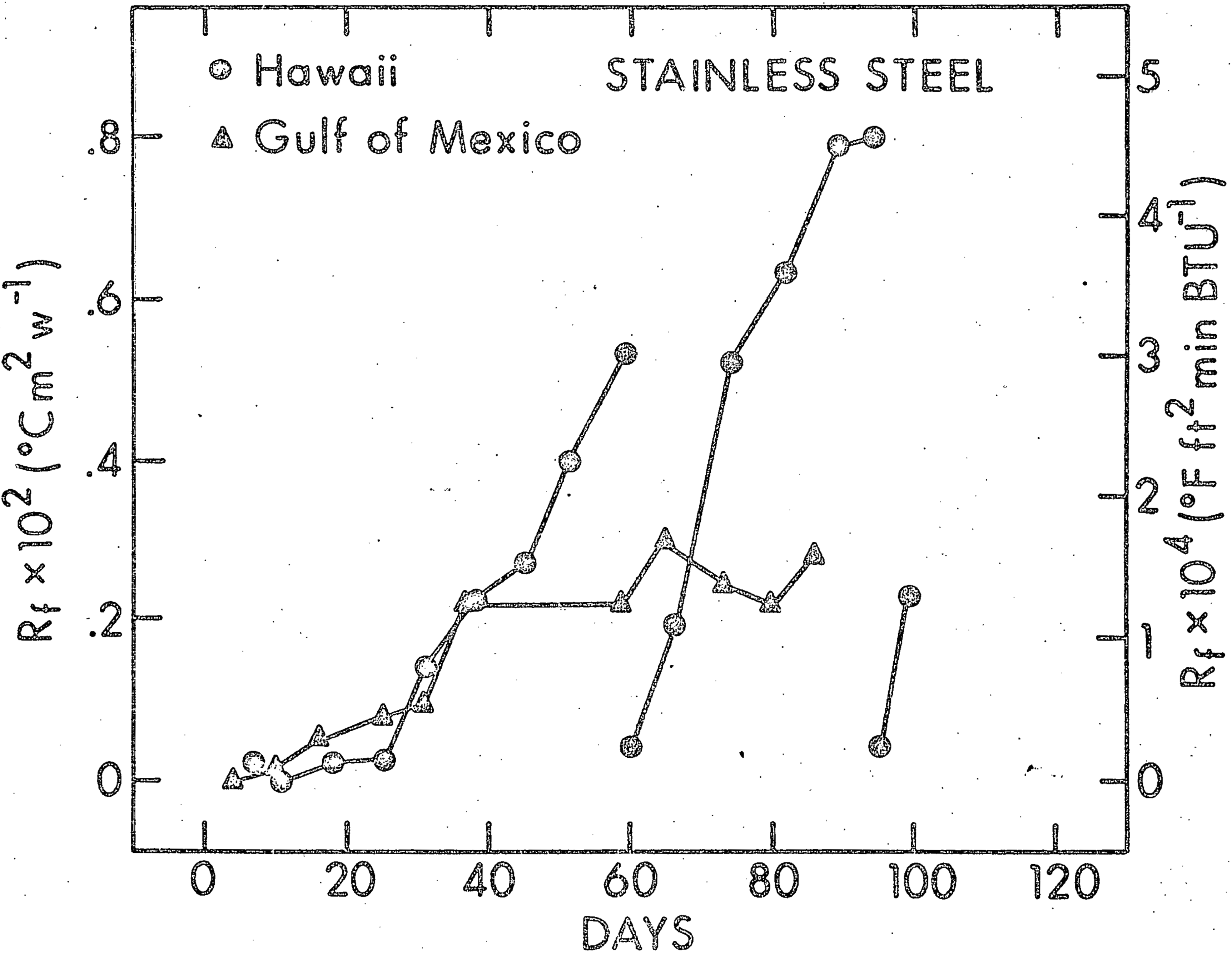

Figure 1b. R_f vs. time for data from the two experimental sites for SS.

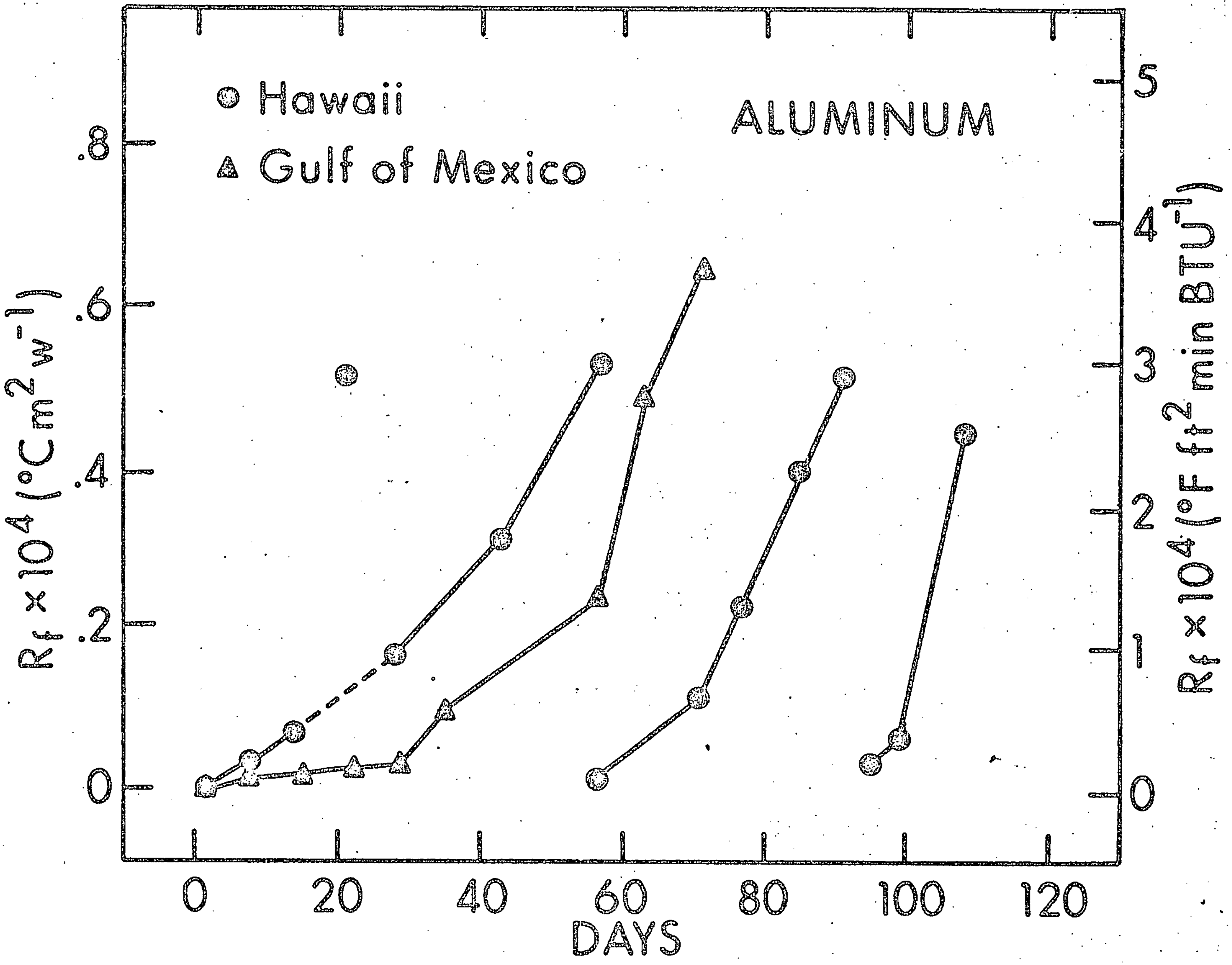

Figure 1c. R_f vs. time for data from the two experimental sites for Al.

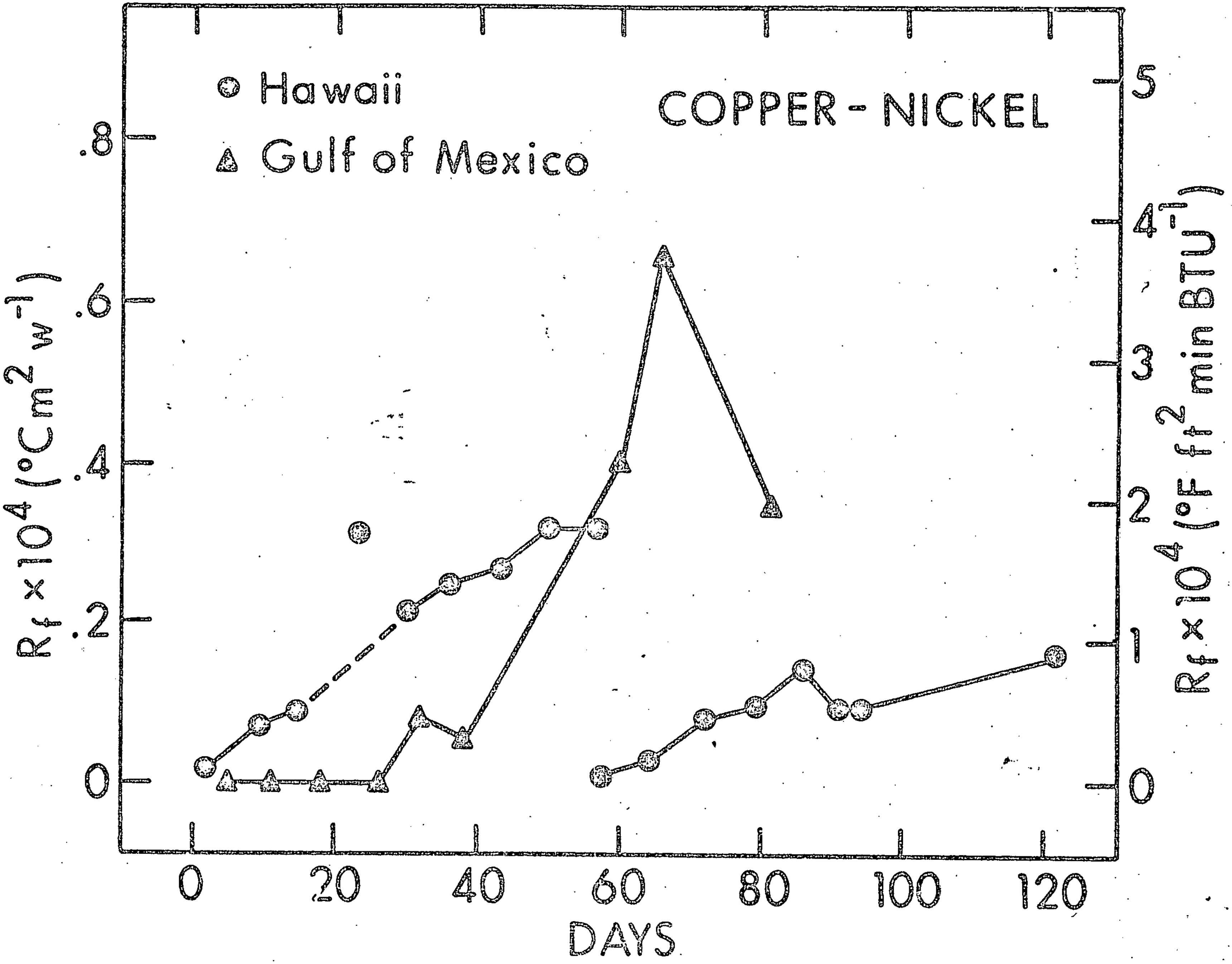

Figure 1d. R_f vs. time for data from the two experimental sites for Cu-Ni.

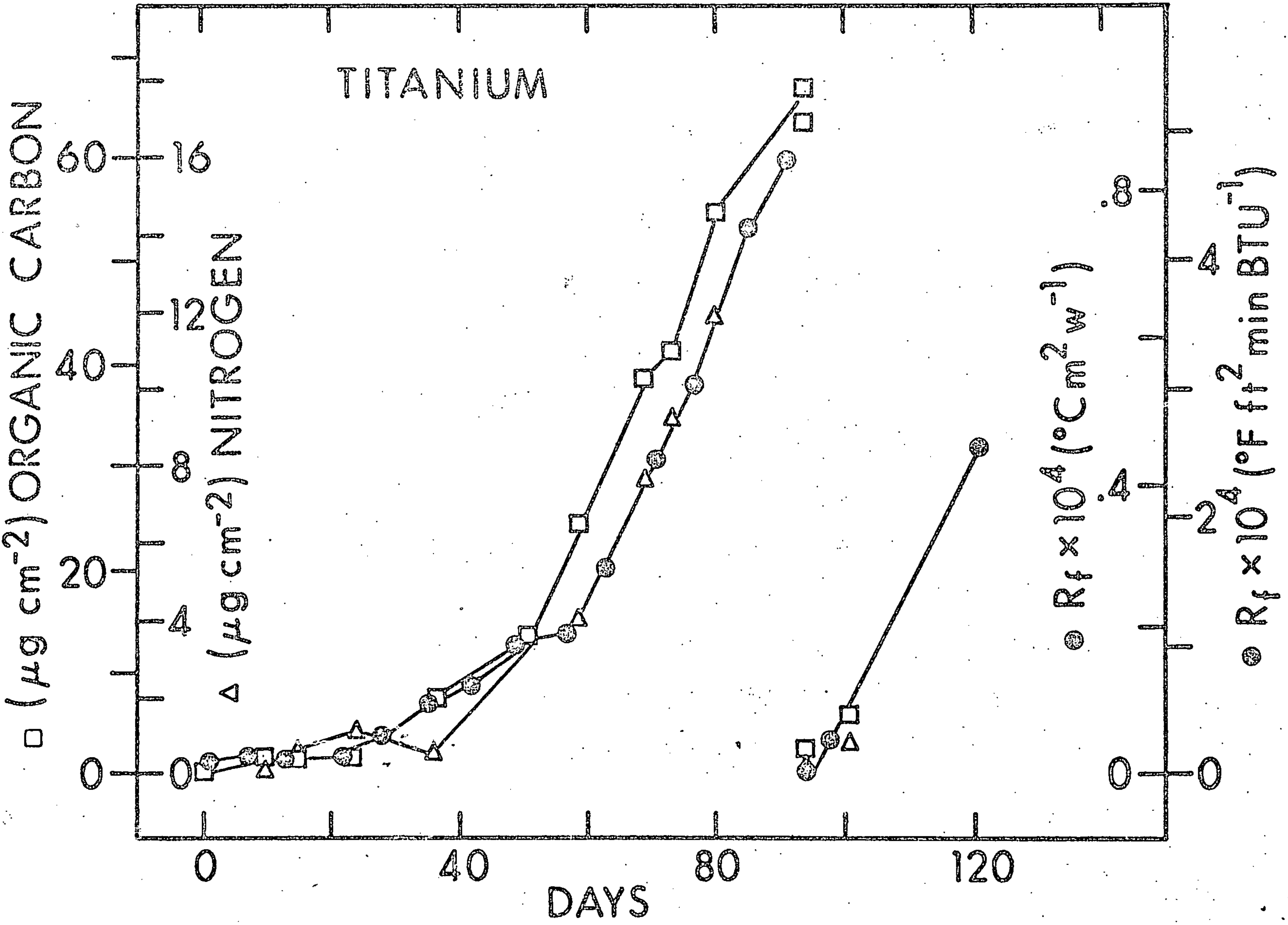

Figure 2a. Total organic carbon, total nitrogen. and R_f vs. time for Ti.

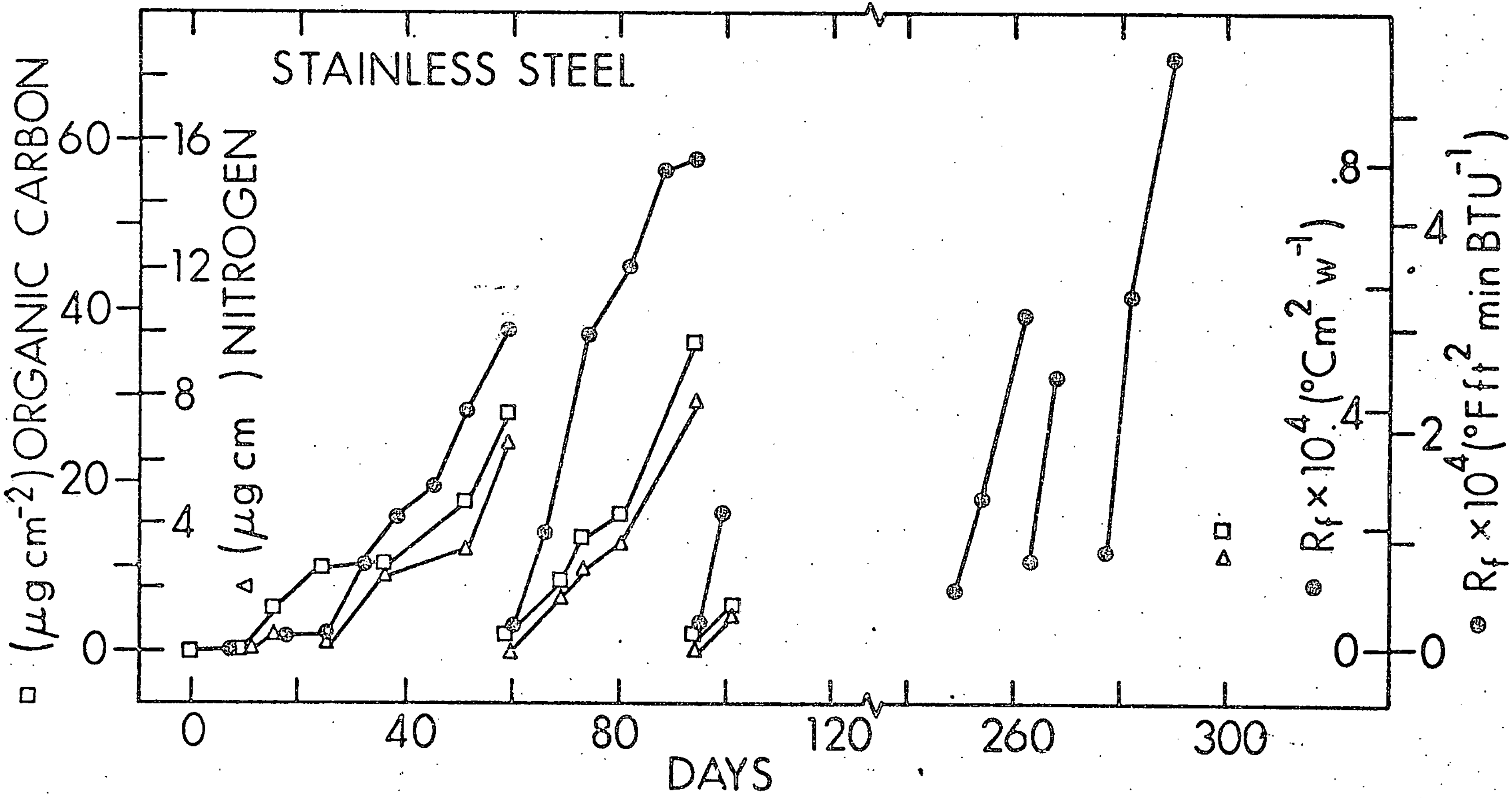

Figure 2b. Total organic carbon, total nitrogne, and R_f vs. time for SS.

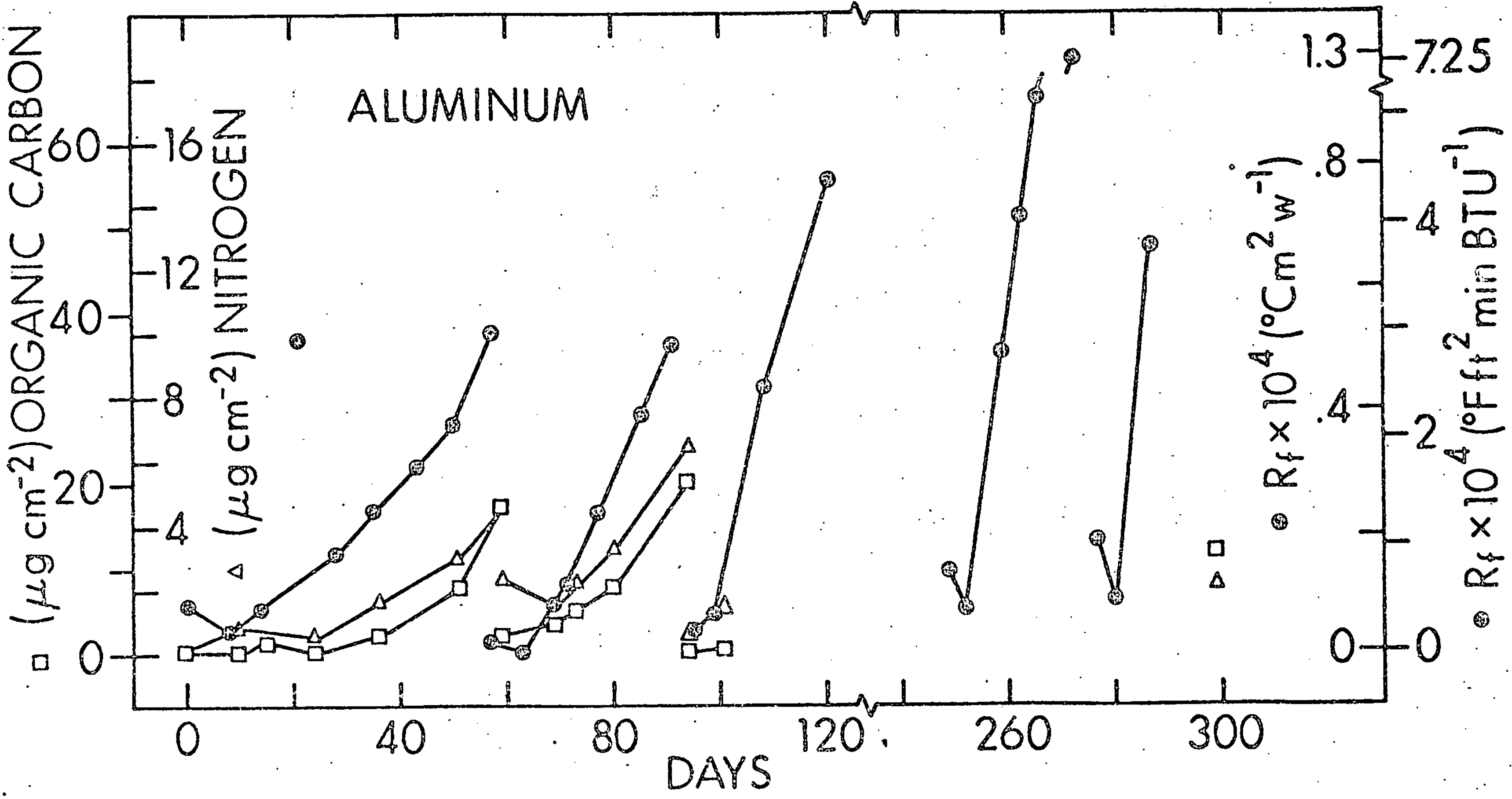

Figure 2c. Total organic carbon, total nitrogen, and R_f vs. time for Al.

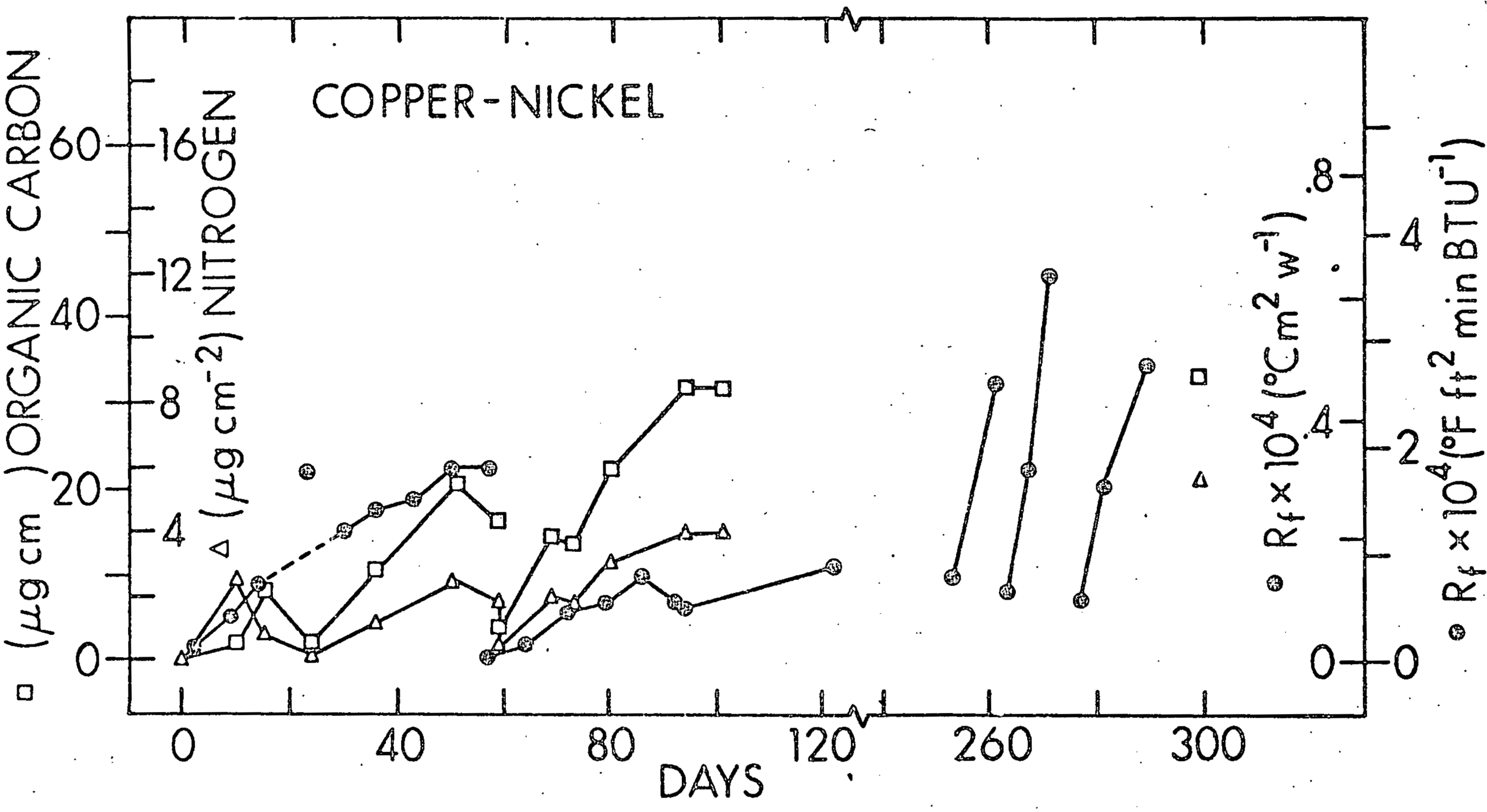

Figure 2d. Total organic carbon, total nitrogen, and R_f vs. time for Cu-Ni.

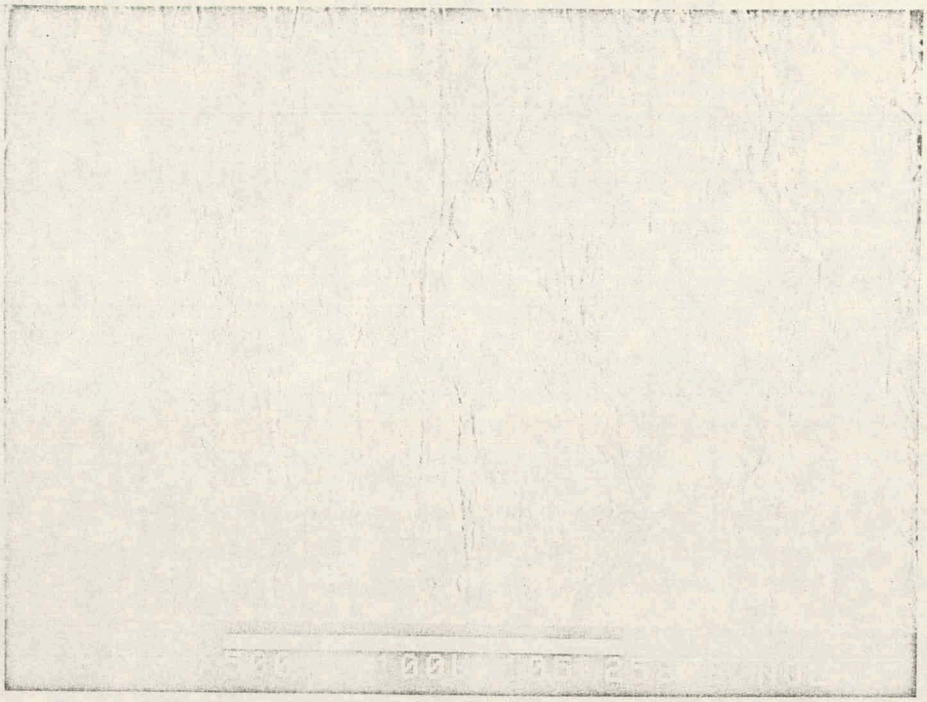

Figure 3a. Zero hour Ti.

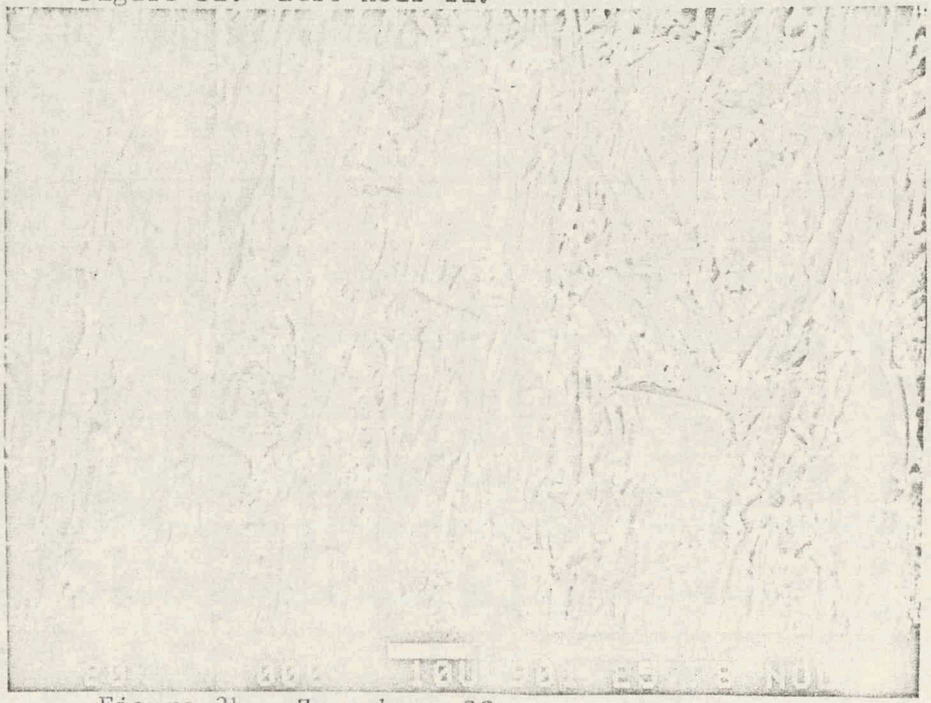

Figure 3b. Zero hour SS.

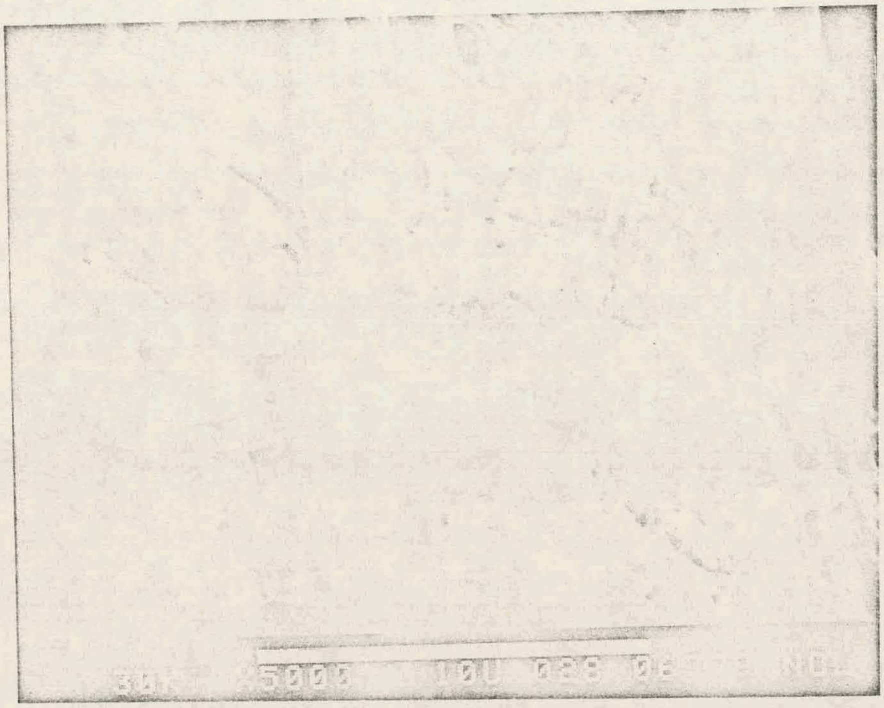

Figure 4. 78-day exposure S.S.

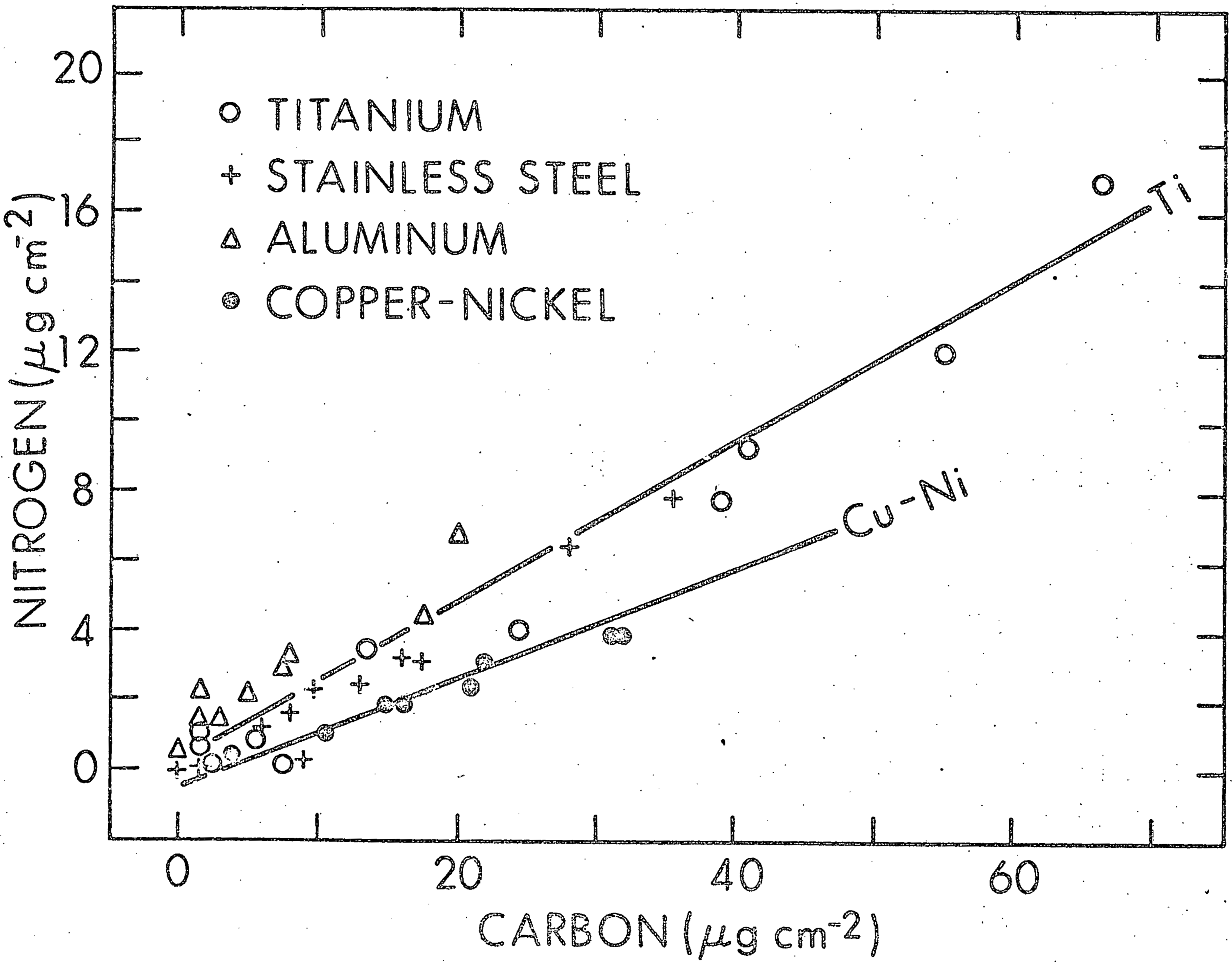

Figure 5. Total nitrogen vs. total organic carbon in the fouling films.

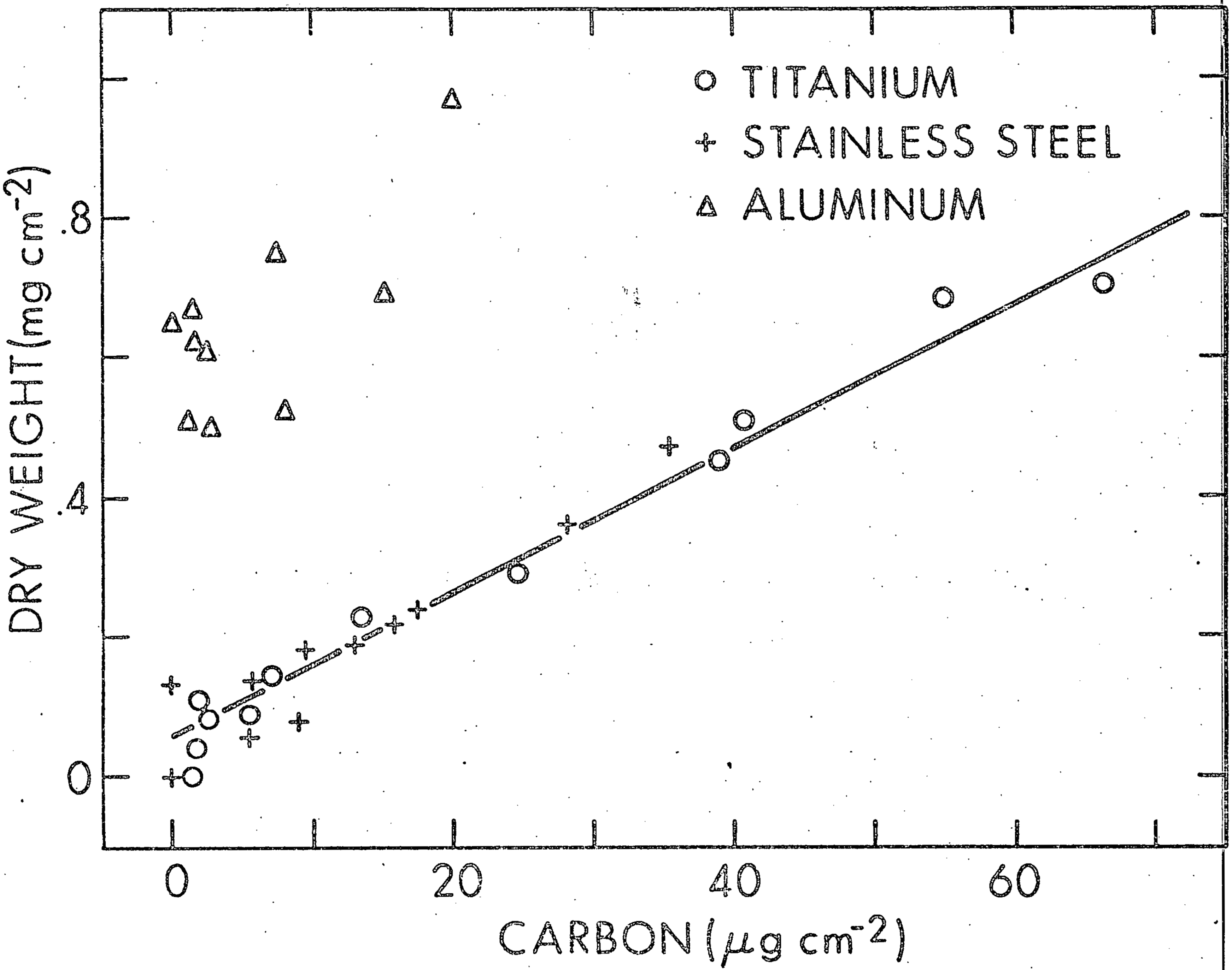

Figure 6. Dry film weight vs. total organic carbon in the fouling films.

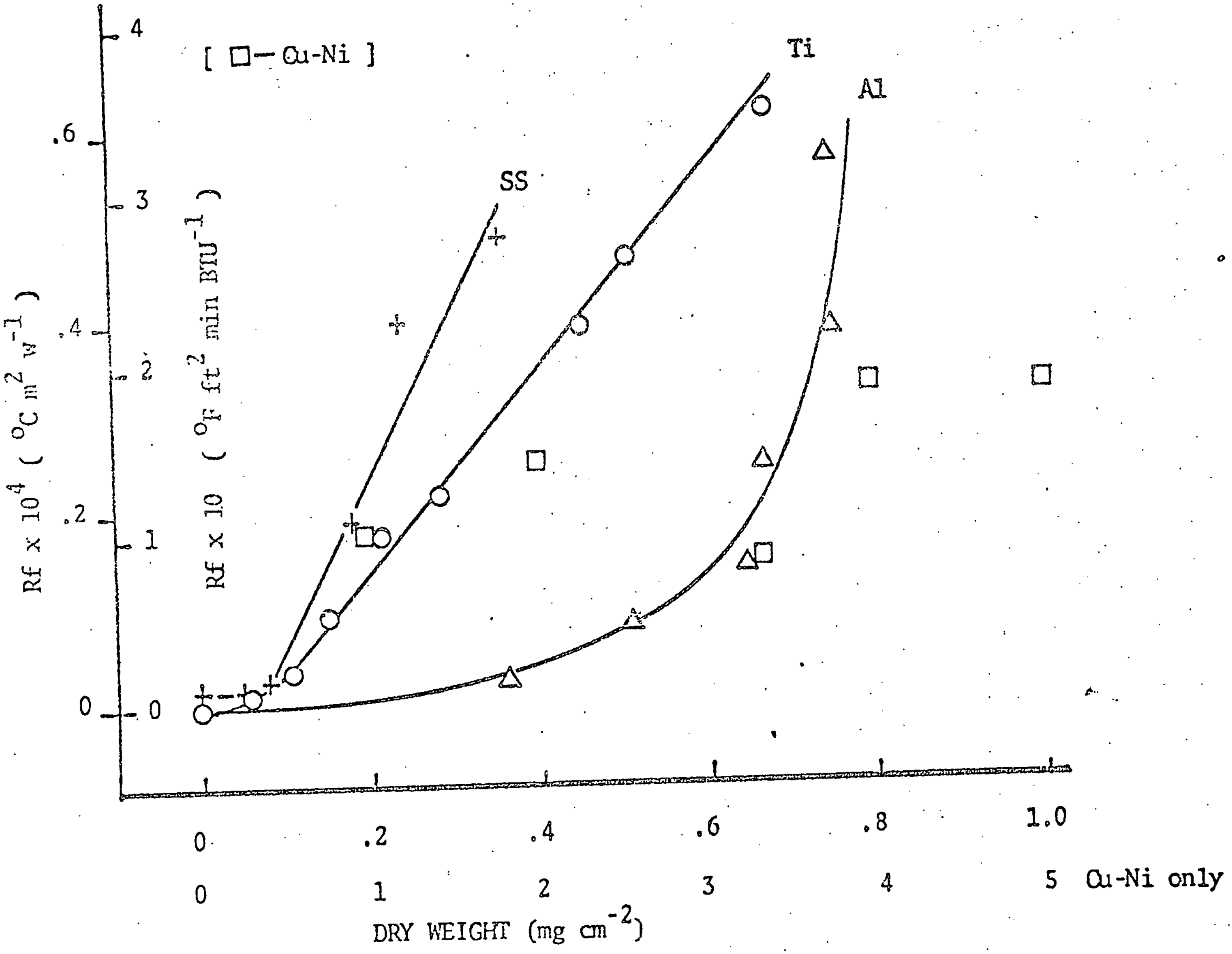

Figure 7. R_f vs. dry film weight.

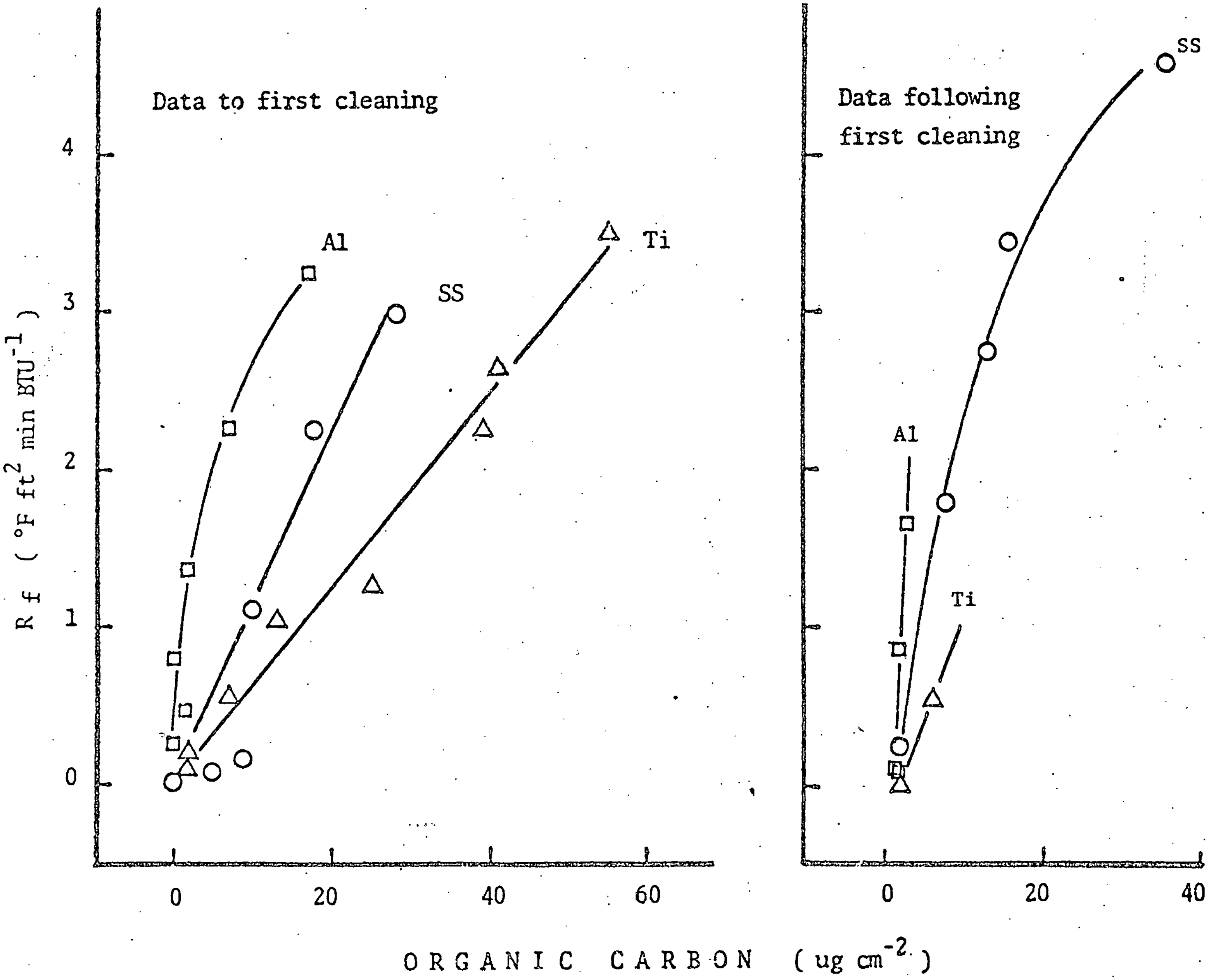

Figure 8. R_f vs. total organic carbon.

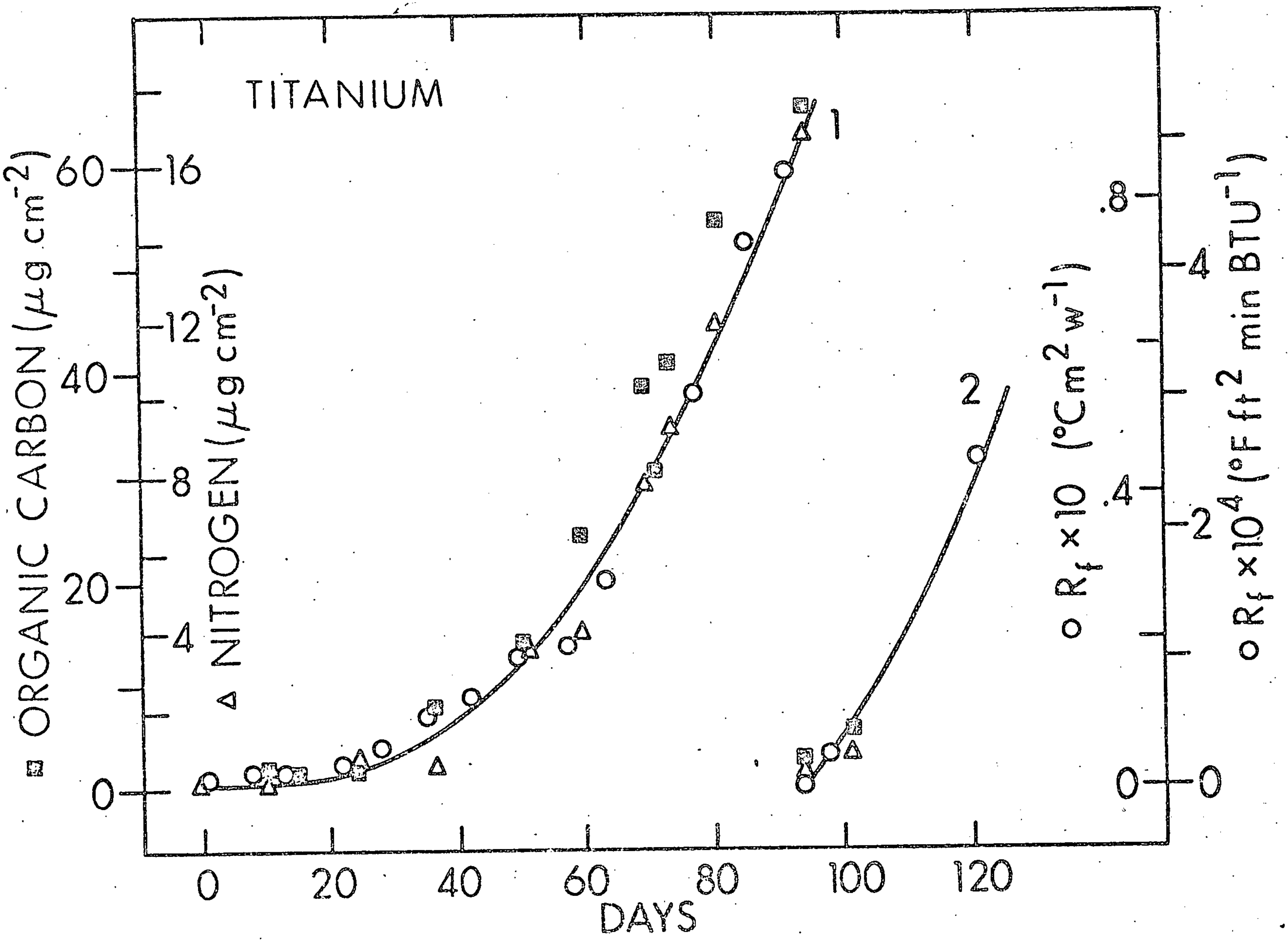

Figure 9a. Total organic carbon, total nitrogen, and R_f for Ti.

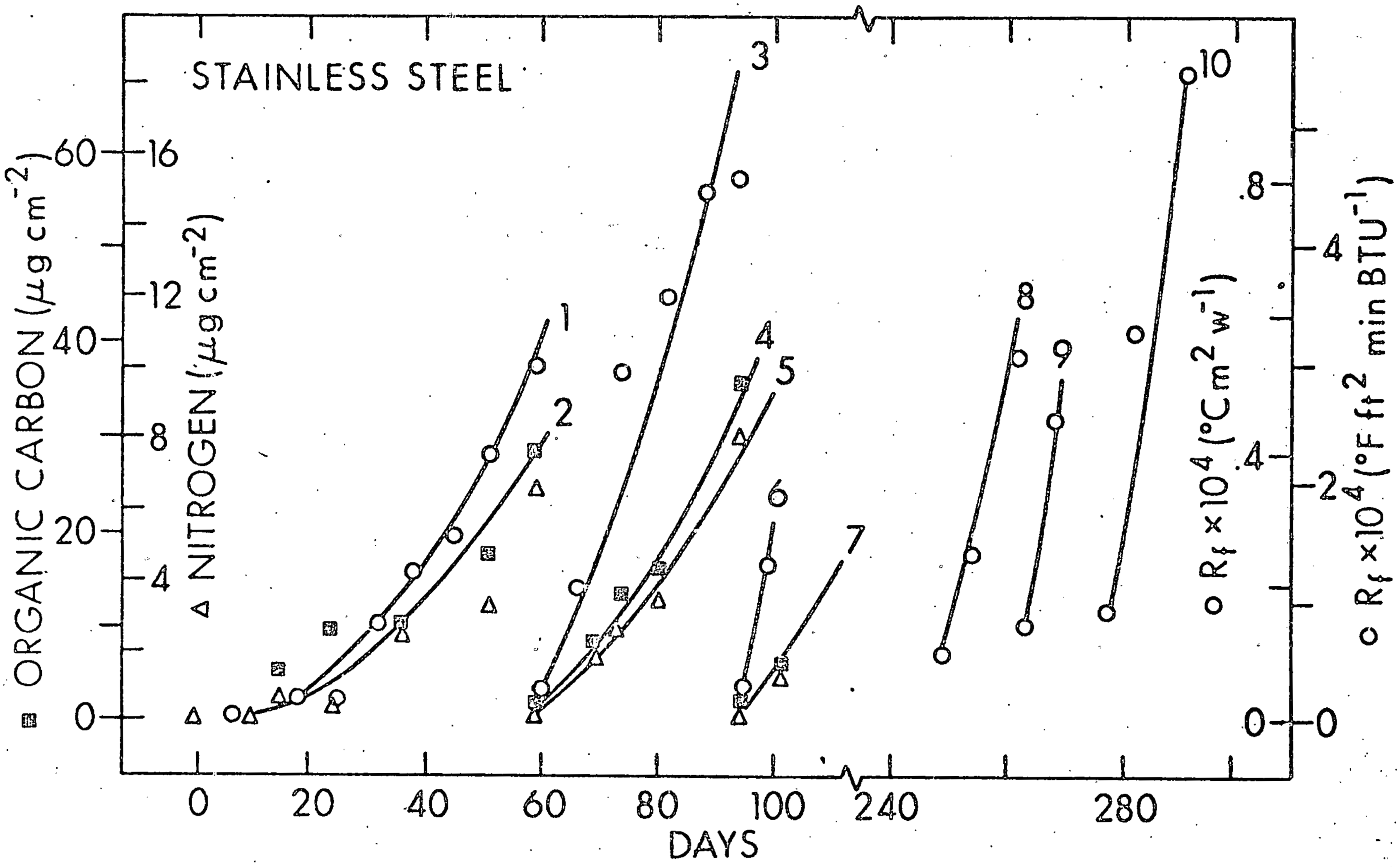

Figure 9b. Total organic carbon, total nitrogen, and R_f for SS.

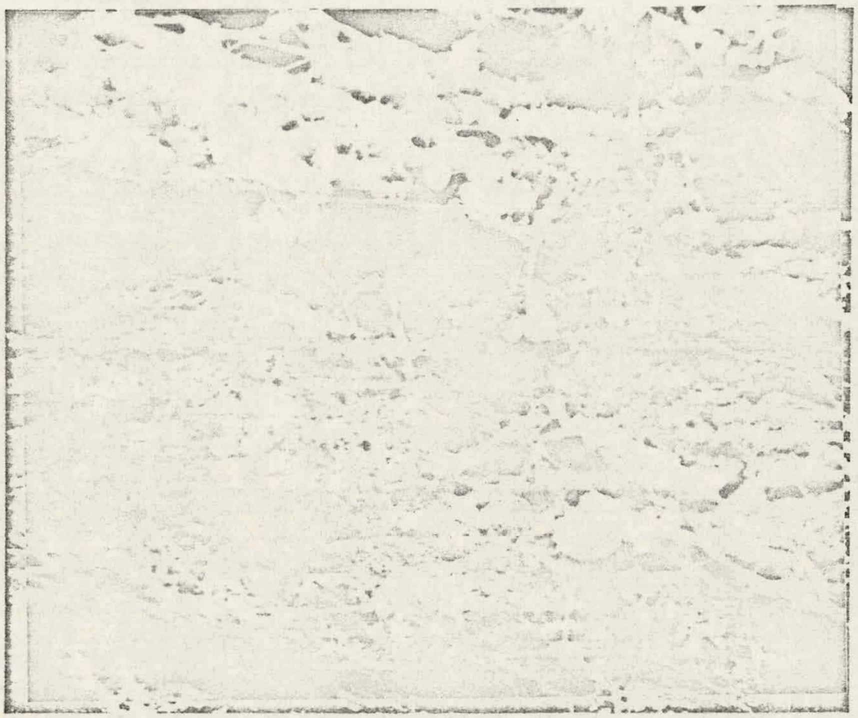

Figure 10. Cu-Ni surface fouled with rod- and filamentous-type microorganisms.

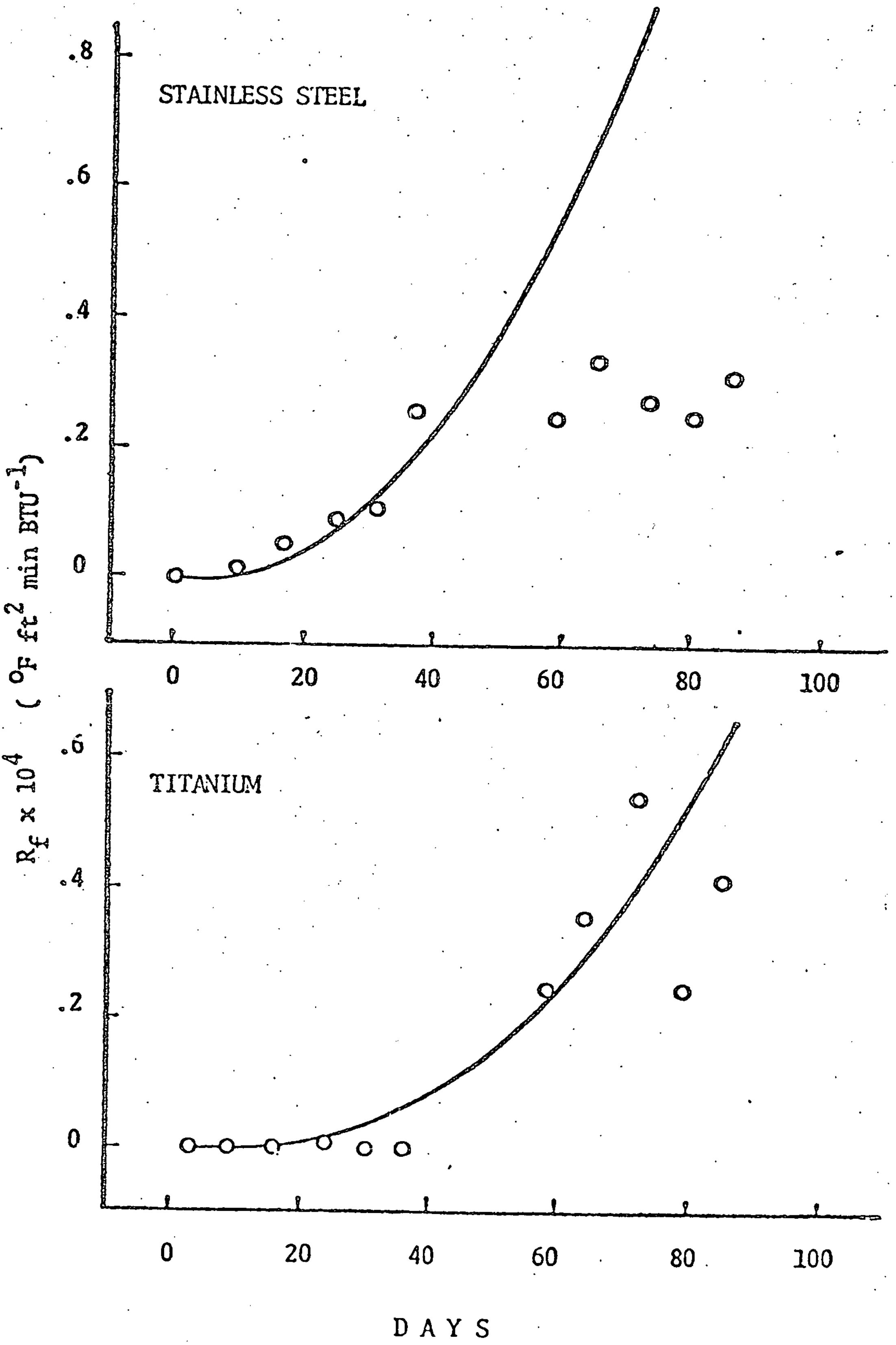

Figure 11. R_f vs. time. Smooth curves generated from model for the Gulf of Mexico experiment.