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TITLE: Corrosion of Copper Base Alloys in a Geothermal Brine

AUTHOR(S): R. L. Miller

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ABSTRACT

The geothermal environment and the experimental procedures and schedules for corrosion tests of copper-base alloys are described. Corrosive attack on these materials was mostly uniform. Some selective leaching of alloying elements was observed, as was crevice corrosion, but the extent of these forms of corrosion was minor. The results of these tests show a trend toward higher corrosion rates with increasing copper content, for the brass alloys. Commercially pure copper, however, showed corrosion rates 20 to 30% of that suggested by the trend in the data. One copper-nickel alloy was tested to verify earlier test data; this alloy showed a corrosion rate about six times that of a brass of similar copper content. The primary agent of the corrosive attack was hydrogen sulfide, present in the water in trace amounts.

The primary conclusion from these tests is that copper-zinc alloys are the most economical materials for boiler and preheater construction. The recommendation is made that materials be selected from these brasses: naval brass, yellow brass, admiralty brass, and copper, in this order of decreasing desirability. Aluminum brass and red brass are marginally acceptable. Copper-nickel alloys are unacceptable for boiler and preheater heat exchangers.

INTRODUCTION

Corrosion is one of the major problems facing those using geothermal resources for power production or for direct applications such as process heat, agricultural stimulation, and space heating. Results of corrosion testing, in the context of materials selection for a demonstration power plant utilizing geothermal fluids as the heat source, are reported here. Corrosion of selected copper-zinc alloys is given particular emphasis.

The resolution of industrial corrosion problems generally involves a combination of materials selection and corrosion inhibitors. Unfortunately, the volumes of water involved in geothermal applications are usually too large to consider chemical means of corrosion control. Further, one must anticipate that any chemical added to the geothermal fluid for corrosion inhibition must be removed prior to fluid disposal to satisfy environmental quality requirements[1]. Thus, materials selction appears to be the most practical approach to corrosion control in most applications of geothermal fluids.

Materials selection for geothermal service based on experience in other applications has not been successful. For example, although data from seawater[2] and desalination[3,4] service would seem to be useful, such technology transfer has been unreliable. In addition, data are generally lacking for materials performance in geothermal environments. The absence of data prompted the Geothermal Project to conduct a series of screening and short-term corrosion tests at the U. S. Department of Energy (DOE) geothermal test site in the Raft River Valley of Southern Idaho. These are engineering tests whose purpose is to provide a materials data base for design of power plant and direct applications facilities at Raft River. The data will permit prediction of the corrosion rates of structural materials and will assist in establishing preventive maintenance schedules and procedures.

Materials performance in geothermal systems is closely tied to materials costs. Earlier tests at Raft River[5] have suggested that the best materials from a corrosion point of view are also the most costly, and are uneconomical for most applications. The least expensive materials are unacceptable from a corrosion standpoint. A middle ground has to be taken, one which appears to involve brasses and bronzes for many applications.

When the proposed 5 MWe power plant at Raft River received approval from DOE, a review of previous Geothermal Project corrosion data was made. This review resulted in the recommendation that admiralty brass be selected for the tubing of the boilers and preheaters of the power plant. Results of corrosion tests conducted to verify the correctness of this material choice support the earlier recommendation.

Reference and illustrations at end of paper.

Copper-nickel alloys, which find wide use in seawater service, do not have sufficient resistance to the geothermal fluid. They are attacked by the hydrogen sulfide in the water. One copper-nickel alloy, 70Cu/30Ni alloy (designation CA 715)[6], was tested to provide a comparison between the present and past tests.

TEST ENVIRONMENT

DOE has drilled seven wells into the Raft River aquifer, but the water used for the corrosion testing reported here has come only from Well No. 1. The temperature of the water from this well was 411 to 414 K (280 to 285°F). Origin of the water in the geothermal aquifer is unknown at this time. Comparisons of the composition of water from this resource with seawater and with water from the Great Salt Lake do not lead to unambiguous conclusions. The best that can be said at this point is that the water resembles seawater that has been diluted by a factor of 10 to 20 times and modified by local, in situ, mineralization.

When evaluating materials response to a corrosion environment, the parameters considered most important are temperature, salinity, pH, content of active gases such as oxygen or hydrogen sulfide, and velocity of the test medium. Metals typically exhibit minimum corrosion at some velocity. For admiralty brass the minimum occurs at about 1.5 m/s (5 ft/s) in seawater[7]. The tests reported here were conducted in geothermal fluid at this flow velocity since heat exchanger design for the boilers and preheaters in the 5 MWe power plant is based on the same value.

Carbon dioxide is a mild oxidizing agent. Its primary influence in geothermal fluids concerns its effect on the solubility of calcium carbonate. The precipitation of calcium carbonate scales on metal surfaces will generally retard corrosion[8-11]. Therefore the effect of carbon dioxide on the solubility of calcite is more important than its action as an oxidizing agent.

The predominant dissolved solid in many geothermal fluids is the chloride ion. The tendency of this species to depolarize metals and to form stable metal/-chloride coordination compounds leads to rapid corrosion of many metals. Other dissolved species may result in accelerated corrosion. For example, oxygen is particularly aggressive, especially in the presence of chloride. The oxygen concentration in the geothermal fluid was measured at 0.25 mg O_2/kg of solution. This amount of oxygen is somewhat greater than that predicted for equilibrium with the minimum 0.1 mg H_2S/kg of solution. The reason for the high oxygen concentration is unknown but may be related to sampling and analysis errors.

The water is nearly saturated with dissolved silica. This substance may cause problems by deposition on heat exchanger surfaces. Butler and Mercer[12] noted that dissolved silica may retard corrosion, but this behavior has not been verified in geothermal systems.

Sulfides, even when present in trace amounts, are very deleterious towards copper-nickel alloys and bronzes containing nickel alloy additions[5,13]. In this respect, data from seawater and desalination service must be used with care since the fluids used in these applications are essentially free of sulfides. Some materials that have performed well in these services have not responded well to geothermal fluids, for example, copper-nickel alloys such as 70Cu/30Ni (CA 715) and 90Cu/10Ni (CA 716).

The Raft River geothermal fluids found to date have sulfide concentrations on the order of 0.1 to 0.2 mg/kg. If all of these sulfides were oxidized to sulfuric acid there would be little change in the pH due to the buffering action of the carbonates in the water.

TEST ASSEMBLY

The tests reported here were conducted in the materials testing portion of the Mobile Components-Test Trailer at Raft River Site 1. The materials test loops are constructed from 10.2-cm (4-in.) Sch. 40 steel pipe. Two 1.22-m (4-ft) test sections are contained in each of the two loops; these are preceded by an instrumented test section and are fitted with flow control and check valves. These two loops may be operated separately, in series, or in parallel. The 1.22-m test sections are joined by Victaulic couplings which permit rapid disassembly and are not as critical, in terms of alignment and length, as screwed fittings.

The two types of samples used in the tests reported here were flat coupons cut from sheet material, and short lengths of tubing. The flat coupons were about 56.6 mm (2.23 in.) in diameter and either 1.6 or 3.2 mm (1/16 or 1/18 in.) thick. A 9.1-mm (23/64 in.) hole was drilled through the center of each coupon for mounting. The tubing samples were 38 or 44 mm (1.5 or 1.75 in.) long and either 19.1 or 22.2 mm (0.75 or 0.875 in.) OD (outside diameter), with various wall thicknessses, according to availability. A 9.5-mm (3/8-in.) diametral hole was drilled through each tube, 1.3 cm (1/2 in.) from one end, for mounting the samples.

The flat corrosion coupons were electrically insulated from each other and from the mounting fixture by polytetrafluoroethylene (PTFE) tubes and washers. The PTFE washers were about 25.4 mm (1.0 in.) OD by 9.8 mm (0.39 in.) ID (inside diameter) and about 5.6 mm (0.22 in.) thick. One side of the washer was beveled about 10° to provide a variable-thickness crevice. The crevice was used to accelerate or encourage crevice corrosion. The tubular samples were mounted using the same type washers and sleeves as for the flat coupons.

The mounting fixture was fabricated from 25.4 x 6.3 x 1200-mm (1.0 x 0.25 x 47-in.) stainless steel bars. The bars were fitted with a cruciform of 6.3-mm (0.25-in.) rods at each end and in the middle to center the bar in the flow chamber. The coupons were mounted so that fluid flow paralleled the face of the coupon.

TEST SCHEDULE

The "Planned Interval Test"[14-16] was used; samples were removed at 35, 70 and 105 days. Additional samples were inserted into the test section for the final 35 days.

The planned interval test schedule offers interesting possibilities for interpretation of corrosion test data. This technique requires four coupons (with replication, additional coupons would be used) for each material to be tested. The general schedule for inserting and removing coupons is shown in Figure 1.

In the planned interval test those variables that can be controlled are held constant for the duration of the test, i.e., from the start of coupon exposure to time = t + 1. Corrosion rates and associated damage are denoted by A_1, A_t, A_{t+1} and B. The corrosion rate A_2 is the difference between A_{t+1} and A_t. In these experiments little or no control of the wellhead temperature or the composition of the geothermal fluid is possible. Changes in either of these variables would contribute to changes in the aggressiveness of the environment. A matrix comparing fluid aggressiveness and the corrodibility of the metal as a function of A_1, A_2, and B is shown in Figure 1.

RESULTS

Weight loss measurements, complemented by visual examinations, were used to evaluate corrosion attack. Visual examinations of the coupons, both before and after cleaning, permitted an evaluation of corrosion product scales as well as the corroded metal surfaces.

The materials of greatest interest in this study were copper and copper-zinc alloys, some with other alloy additions. Aluminum brass (CA 687) and copper-30% nickel (CA 715) were also studied. Weight loss data for all of the copper materials are given in Table I.

Visual examination of the samples showed that a black, corrosion product scale formed over all of the exposed surfaces. The thickness of the scales varied from the tarnish on the most resistant materials to thick, two-layer scales on the most severely attacked specimens. Microscopic examination of these scales shows that they have the same morphology as seen on copper coupons tested previously[3]. X-ray diffraction studies were not conducted on the materials reported here. However, visual examination suggests that the scales are the same as those noted earlier, that is, copper sulfides, copper-iron sulfides, and, in the case of the copper-30% nickel alloy, nickel sulfides.

Small calcite crystals were occasionally found between the PTFE washers and the plate coupons, but not on the tubular samples.

The principal form of attack was uniform corrosion (also termed general corrosion). This was usually accompanied by selective leaching of the zinc. The extent of selective leaching was very small and limited to less than a micron of depth from the surface. Crevice corrosion was evident in some cases although it was minor in all but the copper-30% nickel material.

Weight loss data for the materials show that the first and last five-week test periods resulted in about the same weight loss. This similarity indicates that geothermal fluid aggressiveness toward these materials has not undergone a detectable change during the tests. The weight loss data for these two test periods are plotted as a function of copper content in Figure 2. When presented in this manner the data clearly indicate a decrease in corrosion resistance with increasing copper content. Commercially pure copper does not follow this trend. The observed corrosion rate for copper is only 20 to 30% of that suggested by the trend in the data for brasses. The discrepancy indicates that the corrosion rates must decrease somewhere between 85 and 100% copper. Pure metals frequently exhibit better corrosion resistance than their alloys, but poorer mechanical properties.

The test data were evaluated by regression analysis. Since the tests started using clean coupons, one point on the plot of weight loss as a function of time is zero weight loss at zero exposure time. The least squares method for data constrained to pass through the origin were used to analyze the data[17]. The data for admiralty brass and 70Cu/30Ni were analyzed using linear and parabolic models with the results shown in Figures 3 and 4, respectively.

The fit of the weight loss data for admiralty brass is about as good for the linear model as for the parabolic model. However, when the data for 70Cu/30Ni were fitted to these same models the parabolic model was clearly better.

Analysis of the steps in a corrosion process reveals three potentially rate-controlling processes, viz., diffusion of the corrodant through a solution boundary layer, diffusion of the corrodant through the corrosion product film, and chemical reaction control at the metal surface. Analysis of these processes for flat plates indicates that solution diffusion control should result in linear weight loss as a function of time. Diffusion of the corrodant through a corrosion product layer should show parabolic weight loss as a function of time because the film increases in thickness with time. The chemical reaction should show linear weight loss as a function of time if it is a first-order process.

The data suggest that at long times, indicated by corrosion product films of reasonable thickness, corrosion is controlled by a parabolic process, that is, diffusion through the corrosion product film. This assumption is supported by the data for the 70Cu/30Ni alloy. At short times, when the corrosion product films are very thin, corrosion appears to be controlled by a linear process, either solution diffusion or chemical reaction at the metal surface. Since the corrodant appears to be hydrogen sulfide or some other sulfur species and the concentration of sulfide in the solution is very low, about 0.1 mg/liter, solution diffusion is postulated to be the controlling process.

One of the purposes of these tests was to predict long-term stability from short-term data. The data were analyzed using both the parabolic and the linear models and extrapolated to long times, about 5 years. The results of this analysis for the parabolic case are given in Table I. Because this represents an extrapolation by a factor of more than 17 times, long-term tests are being conducted to verify these predictions and to supply data for extrapolation to the 30-year lifetime of the facility.

CONCLUSIONS AND RECOMMENDATIONS

Copper and brasses are superior to copper-nickel alloys and low-carbon steels for service in hot geothermal fluid. The data for the brasses show a trend toward increasing corrosion rates with increasing copper concentrations. Commercially pure copper shows a corrosion rate of 20 to 30% of that suggested by the trend in the data.

The preferred materials for plant components such as boilers and preheaters are naval brass, yellow brass, admiralty brass, and copper, in this order of decreasing desirability. Aluminum brass and red brass are marginally acceptable. Copper-nickel alloys are unacceptable because of the high corrosion rates resulting from sulfide attack.

The tests to date have been screening and short-term tests to provide a rational basis for materials selection for the 5 MWe power plant and for direct applications of geothermal fluids. The primary feature of the test system was the use of beveled PTFE washers to promote and accelerate crevice corrosion. The samples were examined for this form of attack as well for as selective leaching, pitting, and uniform corrosion. Future tests will be modified to include test configurations to evaluate the contribution of galvanic action to the corrosion process.

Aeration typically increased corrosion rates. However, in the presence of sulfides the corrosion rates may decrease since the primary aggressive species in the Raft River geothermal water for copper materials is hydrogen sulfide. Sulfides may be oxidized to relatively nonaggressive sulfur species by the action of oxygen in the air[18]. The effect of brine aeration is being studied at this time.

Tubular samples were included in the present series of tests because of previously observed differences in corrosion between plate and tubing samples exposed to the geothermal fluid. The plate showed greater corrosion than did tubing specimens sectioned from heat exchanger test materials. The data from the present test do not show any significant difference in these two configurations. The conclusion reached is that the previously observed differences were due to the lower temperatures experienced by the heat exchanger tubes.

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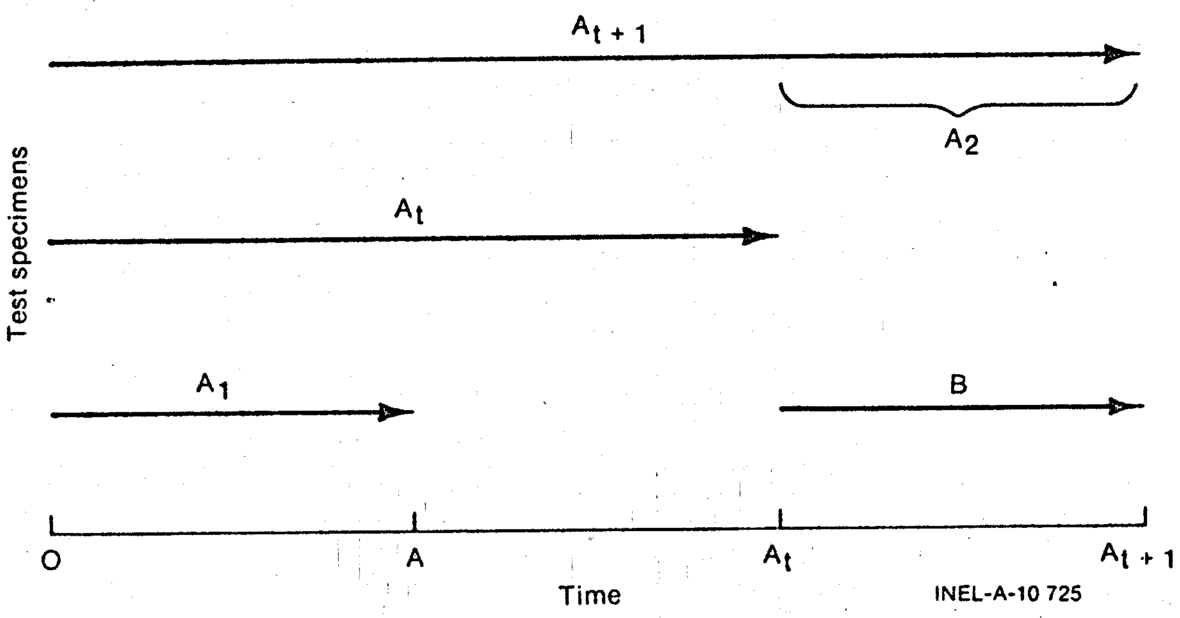
TABLE I

CORROSION BEHAVIOR AS A FUNCTION OF TIME FOR COPPER-BASE MATERIALS

Material	Weight Loss, mg/cm^2					Predicted Weight Loss in 5 years, mg/cm^2	Predicted Reduction of Thickness in 5 years, mm
	1st 5 weeks A_1	Last 5 weeks B	10 weeks A_t	15 weeks A_{t+1}	15 weeks - 10 weeks A_2		
Copper Plate	7.08	16.56	21.03	28.59	7.56	117	1.31
Copper Tube	8.81	7.57	29.14	38.51	9.37		
Red Brass Plate	18.57	20.40	36.95	48.51	11.56	182	2.08
Aluminum Brass Plate	12.15	12.26	26.25	35.29	9.04	126	1.51
Admiralty Brass Plate	7.01	7.64	12.86	11.66	-1.05	60.7	0.711
Admiralty Brass Tube	6.71	7.84	13.84	17.68	3.84		
Yellow Brass Plate	3.90	4.46	8.27	7.64	-0.63	29	0.342
Naval Brass Plate	2.64	2.67	3.76	5.45	1.69	21	0.250
Copper, 30% Nickel Plate	61.26	63.78	83.22	100.75	17.53	440	4.92
Copper, 30% Nickel Tube	62.21	64.38	94.43	103.11	8.68		



	Liquid corrosiveness		
Metal corrodibility	Decreased	Unchanged	Increased
Decreased	$A_2 < B < A_1$	$A_2 < A_1 = B$	$A_1 < B > A_2$
Unchanged	$A_2 = B < A_1$	$A_1 = A_2 = B$	$A_1 < A_2 = B$
Increased	$A_1 > B < A_2$	$A_1 = B < A_2$	$A_1 < B < A_2$

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Fig. 1 - Planned interval test scheduling and interpretation. A. Schedule for exposure according to planned interval test sequence. B. The interrelationship of selected weight loss data from planned interval testing.

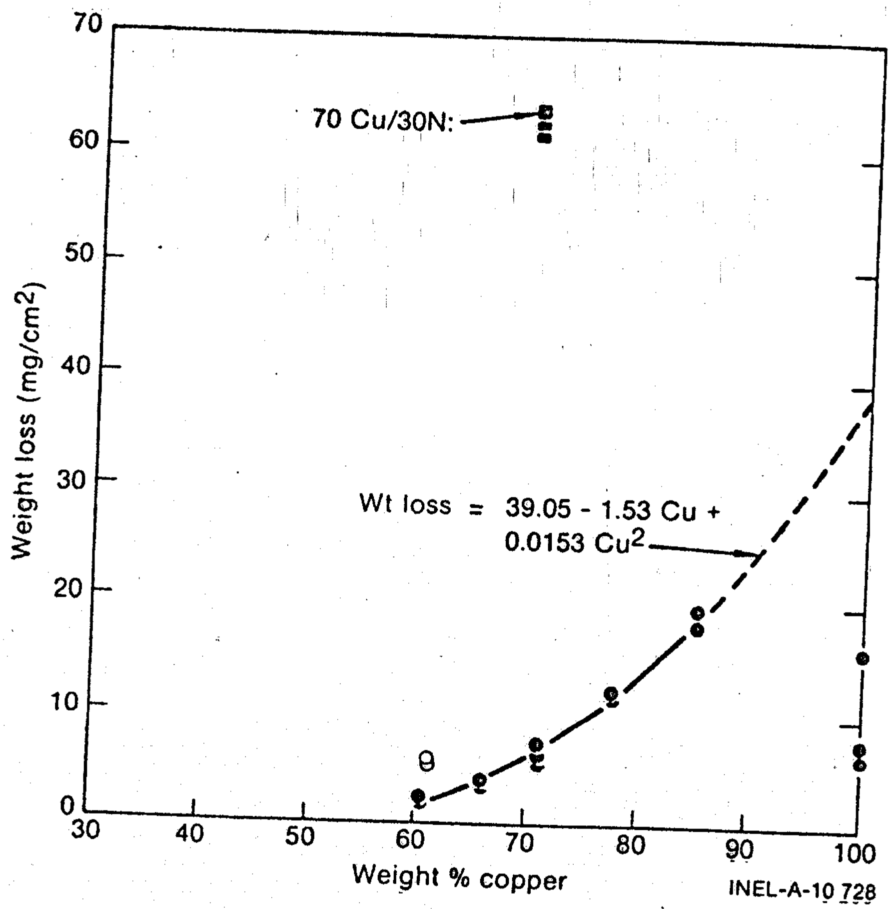

Fig. 2 - Weight loss in 5 weeks for selected copper alloys exposed to geothermal fluid as a function of copper content.

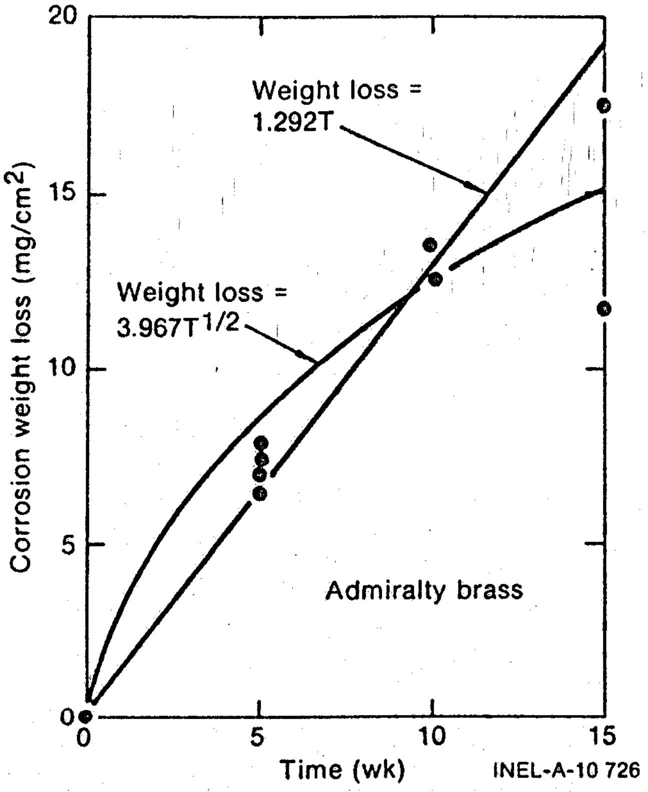

Fig. 3 - Weight loss of admiralty brass exposed to geothermal fluid as a function of time.

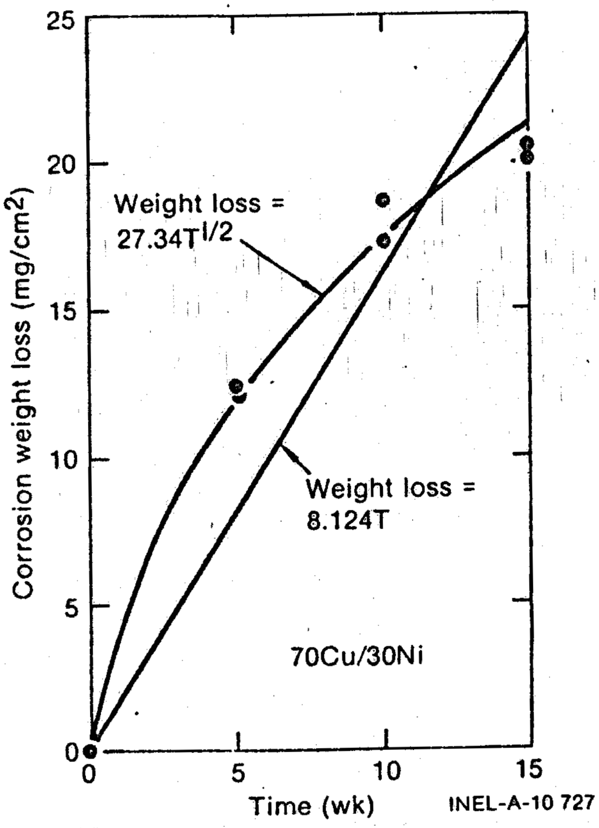

Fig. 4 - Weight loss of 70Cu/30Ni alloy exposed to geothermal fluid as a function of time.