

November 29, 1989



UNITED STATES DEPARTMENT OF COMMERCE
National Institute of Standards and Technology
[formerly National Bureau of Standards]
Gaithersburg, Maryland 20899

Mr. Charles H. Peterson
Engineering Branch
Division of High-Level Waste Management
Office of Nuclear Materials Safety and Safeguards
U.S. Nuclear Regulatory Commission
Washington, DC 20555

Dear Mr. Peterson:

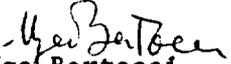
In response to your request of November 27, 1989 for general technical assistance under Task 4 of FIN 4171, comments on the paper titled, "Degradation Modes in Candidate Copper-Based Materials for High-Level Radwaste Canisters", by H. K. Manaktala are given below.

Let's begin by saying that there is nothing particularly bad with this paper. It is a fairly diligent collection of the corrosion literature on copper. However, its value is limited because the author simply reports the observations and conclusions of the investigations reviewed and fails to provide any unique or inspiring insight on the problems related to the use of copper based alloys for HLW disposal.

Specific points are:

- 1) A number of typos, spotted during reading, have been marked in yellow.
- 2) A sentence at the bottom of p. 11, does not seem to make sense. It has been probably taken from some reference, and should be rephrased so as to make it meaningful.
- 3) There are some points where a reference would be desirable. Examples are the discussion of SCC in Cu-Ni alloys (p. 9, next to last paragraph) and the whole section dealloying.
- 4) The discussion of the effects of radiation seem to be particularly deficient. The formation of nitrogen oxides, and their possible consequences, both in the gas and in the liquid phase, is hardly touched. The role of hydrogen peroxide, for instance, is never discussed. This seems particularly odd, since the section "DEGRADATION OF COPPER-BASED ALLOYS UNDER RADIATION" (p. 12), sounds, on the other hand, as a too detailed retelling of the papers of Yunker and coworkers.

Sincerely,


Ugo Bertocci
Corrosion Group
Metallurgy Division

Enclosure

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DEGRADATION MODES IN CANDIDATE COPPER-BASED
MATERIALS FOR HIGH-LEVEL RADWASTE CANISTERS

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ABSTRACT

Copper and copper-based alloys (aluminum bronze and cupro-nickel) are being considered for the HLW canisters for a deep geologic repository. This paper reviews the literature published on the degradation modes of these materials in a variety of environments and discusses the significance of the known failure mechanisms to the Yucca Mountain, Nevada, repository application. Areas requiring additional specific experimental work to generate information for understanding the degradation mechanisms of interest and for modelling and predicting long-term behavior of these materials for the period of interest, which spans thousands of years, are identified.

*good no suggestions just
identification*

INTRODUCTION

The U. S. Department of Energy (DOE) is in the process of selecting a material(s) for the HLW canisters for the proposed deep geological repository in the Yucca Mountain, approximately 120 miles northwest of Las Vegas, Nevada. In its selection of the canister material(s) the DOE is guided by the regulatory requirements governing containment, retrievability of the waste packages, and gradual release upon eventual breach of the waste package [1]. Based on its initial studies on materials, the DOE reduced the number of the primary candidate materials from 18 to 6. Using information about the degradation modes of these six candidate materials from the literature and through conducting tests in environments appropriate to the Yucca Mountain repository, the DOE is expected to narrow this list to one or two materials for in depth investigation to evaluate the suitability of the chosen material(s) for fabricating HLW canister. The present list of six candidate materials belong to two different classes, viz. the austenitic materials (two stainless steels and a high nickel-chromium alloy) and copper-based alloys (copper, aluminum bronze, and cupro-nickel).

DEGRADATION OF A MATERIAL IN THE CONTEXT OF
THE YUCCA MOUNTAIN HLW REPOSITORY

Degradation of a material usually means the "compromise" of the material in some way rendering it incapable of meeting its intended function. In the context of the Yucca Mountain repository, the ultimate interest is to determine which of the three candidate copper-based materials can meet the intended function of providing containment for ~~the~~ the radioactive inventory within the canister. How accurately one can assess whether the canister fabricated from the chosen material can meet the requirements, without conducting full-scale full service duration test (literally impossible to do), depends on the the accuracy of the information pertaining to the service environment (and how it might change with time over the entire period of interest), the design of the canister and the nature of its contents, fabrication techniques used for the canisters, and understanding of the degradation modes & kinetics of the processes involved. Each of these areas influences others in a variety of ways. Therefore, the process of determining the suitability of a material, for a particular application, is an iterative process. Such will, also, be the case in evaluating HLW canister material(s) for the Yucca Mountain repository. The scope of this paper is limited to survey of the literature reported degradation modes of copper and copper-based alloys, drawing preliminary conclusions regarding the possibility of those degradation mechanisms being life limiting in the Yucca Mountain repository environments, and, ~~where possible~~ ^{where possible}, some focused experiments to fill in the missing technical information essential to the materials evaluation process for the HLW canisters.

COPPER-BASED ALLOYS BEING CONSIDERED FOR THE HLW CANISTERS

The copper-based alloys being considered for the HLW canisters for the Yucca Mountain repository are alloys CDA102, CDA 613, and CDA715. The CDA102 is essentially an unalloyed oxygen-free copper, CDA613 is a single alpha-phase binary of 7 w/o aluminum with balance of copper, while CDA715 is a solid solution of 30 w/o nickel in copper. The chemical composition of these alloys are provided in Fig. 1 [2,3].

DEGRADATION MODES OF COPPER & COPPER-BASED ALLOYS

Copper and copper-based alloys, like most other metals & alloys, are susceptible to several forms of degradation, depending primarily on environmental conditions. Because of the characteristics and the geochemical environment of the Yucca Mountain repository site [4], understanding of both oxidation and corrosion phenomena, as related to the three candidate alloys, in gas, vapor, and aqueous phase (including the unique chemical and radiation environment that may exist in the repository), is essential. Since there is no existing HLW deep geological repository where copper and copper-based alloys have been used as canister materials, most of the failure mechanisms identified in the literature for copper and copper-based alloys are in service

environments not quite like the one expected in the Yucca Mountain repository [4]. Nevertheless, some important conclusions can be drawn from the literature, regarding mechanisms that need to be understood well in order to model and predict long-term performance of these candidate alloys in the repository environment.

LITERATURE REVIEW

Corrosion in Gases

but may contribute to HLW canister degradation in repository environment

The gases ~~that are important from the HLW canister point of view~~ are oxygen and nitrogen (which are present in the air), and hydrogen which might be generated by the radiolysis of the moisture that may be present in the repository during the early part of the container life. Nitrogen in molecular form is essentially inert and is not expected to react with candidate canister materials.

Air/Dry Oxygen. When copper is heated in air, it develops a Cu_2O film that exhibits a series of interference tints (temper colors) as it increases in thickness [5]. Black cupric oxide (CuO) forms over the Cu_2O layer as the film thickness increases above the interference color range. Scaling results when copper is used at elevated temperatures in air or oxygen [5]. At low temperatures (up to $100^{\circ}C$), the oxide increases in thickness logarithmically with time. Beyond the interference color range, the growth rate of the oxide film is approx. defined by:

$$W^2 - kt \dots\dots\dots (1) \quad [5]$$

where W is the weight gain per unit area,
t is the time, and
k is a constant of proportionality

Values of k are available in the literature [5,6]. The rate constants reported for oxide growth on unalloyed copper in air are lower than for pure oxygen [5].

In the repository environment the conditions during the early part of the canister life are expected to be dry [4]. During this time period, the canister surface temperature, for the spent fuel canister, is expected to be $>150^{\circ}C$ for the first 100+ years and then level-off to slightly above $100^{\circ}C$ for the next 1000+ years [4,7]. For the canisters containing vitrified waste, the temperatures are expected to be much lower, ranging approx. $130^{\circ}C$ to $95^{\circ}C$ for the first 100+ years and then levelling-off to below $60^{\circ}C$ after about 1000 years [4,7]. Under these circumstances some oxidation leading to discoloration of the canister can be expected, with possibly some scaling-off of the spent fuel canisters. The oxide scale on the spent fuel canisters could be irregular at temperatures above $100^{\circ}C$ [5]. All three candidate alloys are expected to respond to the air/oxygen environment in a similar way, however the oxide growth/scale kinetics could be different.

Hydrogen. Copper and its alloys are not usually susceptible to attack by hydrogen unless they contain copper oxide [5]. When oxygen-bearing copper is heated in hydrogen or hydrogen-bearing gases, the hydrogen diffuses into the metal and reacts with the oxide to form water, which is converted to high-pressure steam if the temperature is above 375°C. The steam produces fissures, which decrease the ductility of the metal. This condition is generally known as hydrogen embrittlement. A high degree of embrittlement can lead to catastrophic failure and therefore should be avoided. There is no safe depth of attack [5]. When copper must be heated in hydrogen atmospheres, an oxygen-free copper or deoxidized copper with high residual deoxidizer content is recommended. No hydrogen embrittlement problems have been reported with these grades of materials [5].

The copper grade being considered for the HLW canister, CDA102, is an oxygen-free grade. The temperature of the canisters is not expected to exceed 275°C any time during the life of the canister in the repository [4,7]. Therefore, hydrogen embrittlement is not expected to be a problem for the HLW canisters.

Corrosion in Steam

Copper and copper-based alloys resist attack by pure steam, but if much CO₂, oxygen, or NH₃ is present, the condensate is corrosive [5]. Such a situation may arise in the repository due to radiolysis of water vapor (saturated with air) present in the repository. Besides hydrogen, the radiolysis process could be expected to generate some NH₃ and other nitrogen compounds. These chemical species could lead to stress corrosion cracking (SCC) if tensile stresses are present in the canister. Besides the possibility of residual stresses from the canister fabrication processes, another source of high-level of residual stresses is the closure weld, if welding is used for the canister lid closure and it is not given proper post-weld heat treatment.

A few copper-based alloys have shown a tendency to fail by SCC when they are highly stressed and exposed to steam. Alpha aluminum bronzes that do not contain tin are among the susceptible alloys [5]. The aluminum-bronze grade being considered for the Yucca Mountain repository (CDA613) contains 0.2 to 0.5% tin and is, therefore, expected to be immune/less susceptible to SCC in steam than other grades containing no tin [5,7]. The alloy CDA715 is reported to be susceptible to IGSCC when exposed to steam at 350°C even in the absence of applied stress [8]. Accelerated intergranular attack can occur at certain threshold stress, the value of which appears to depend on the chemical composition of the alloy and its metallurgical condition [8].

Corrosion in Aqueous Environments

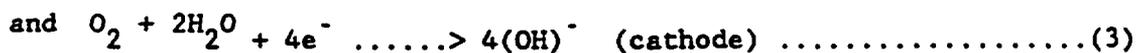
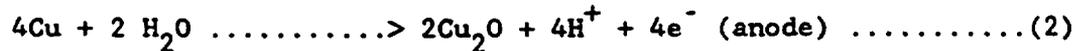
During the later part of the canister life, approx. 1000 years after emplacement of the spent fuel in the repository, and about 100 to

150 years after emplacement for the vitrified waste containers, the canister temperature is expected to drop below the boiling point of water [7]. At that time degradation of the canister is expected to be primarily due to corrosion in the aqueous phase (assuming that water will intrude the repository at that time). Depending on the chemical species present in the aqueous phase, the geometry of the canister and its surface flaws/defects, crevices, etc., and the properties of the oxide layer already present on the canister and its rupture and regenerative behavior, the canister can undergo various forms of materials degradation. Since the dominant degradation mode in the aqueous phase will depend on several variables, some of which are listed above and are not known about the Yucca Mountain repository at this time with a great precision, the discussion about the degradation of the candidate HLW canister material in aqueous phase is provided in general terms.

The types of corrosion of the metals in the aqueous media can generally be classified into eight forms, based upon the appearance of the corroded metal [9,10]. These are: uniform corrosion, pitting corrosion, crevice corrosion, galvanic corrosion, stress corrosion, erosion corrosion, fretting corrosion and dealloying (selective leaching). Given long enough exposures and appropriate environment, all eight types of corrosion listed above have been observed in copper and its alloys [5]. Of the types of corrosion listed above, the most significant for the HLW canister degradation in the Yucca Mountain environment are considered to be: uniform corrosion, pitting corrosion, crevice corrosion, galvanic corrosion, dealloying (selective leaching), and stress corrosion ~~cracking~~. These forms of corrosion, and how they may impact the candidate HLW canister material in the repository, are reviewed below.

stress corrosion cracking is not listed as one of the previous identified eight.

Mechanism of Aqueous Corrosion. Copper and its alloys are unique among the corrosion-resistant alloys in that they do not form a truly passive corrosion product film. In aqueous environments at ambient temperatures, the corrosion product predominantly responsible for protection is cuprous oxide (Cu₂O). This Cu₂O film is adherent and follows a parabolic growth kinetics [5]. Cuprous oxide is a p-type semiconductor formed by the electrochemical process:

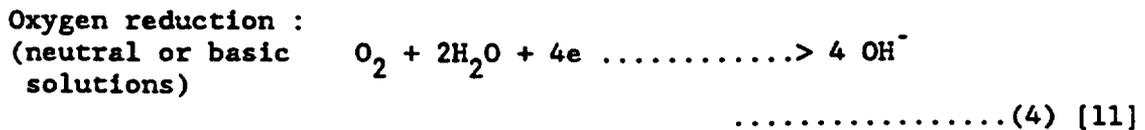


with the net reaction: $4\text{Cu} + \text{O}_2 \dots\dots\dots > 2\text{Cu}_2\text{O}$.

For the corrosion reaction to proceed, copper ions and electrons must migrate through the Cu₂O film. Consequently, reducing the ionic or electronic ~~conductivity~~ conductivity of the film by doping with divalent or trivalent cations should improve corrosion resistance. In practice, alloying additions of aluminum, zinc, tin, iron, and nickel are used to dope the corrosion product films, and they generally reduce corrosion rates significantly [5]. Based on this explanation, the two copper-based alloys being considered for the HLW canisters should form oxide films,

in aqueous solutions, which are more protective (corrosion resistant) than can be expected on pure copper (CDA102).

Corrosion in Water. Since copper is not an inherently reactive metal, the general rate of corrosion in water even in the absence of corrosion films or insoluble corrosion products is usually low. Nevertheless, in practice, the good behavior of copper and its alloys often depends to a considerable extent on maintenance of a protective oxide film. When copper corrodes in near-neutral water, the controlling cathodic reaction is one of oxygen reduction according to eqn 4 [11].



The oxide film formed in water is generally cuprous oxide (Cu₂O), but, under more oxidizing conditions, cupric oxide (CuO) is the stable form as shown, in Fig 2, in the potential-pH equilibrium diagram for the system copper-water [12]. The kinds of attack that are observed in aqueous environments can be broadly classified as (i) general, or (ii) localized. There are many types of localized corrosion. The ones that are considered important for the HLW canisters are: pitting, crevice, dealloying, galvanic, and stress corrosion.

General Corrosion. This type of corrosion is characterized by well-distributed attack of an entire surface with little or no localized penetration. It is the least damaging of all forms of attack, easy to predict and account of while designing a component for an application where this is the dominant mode of materials degradation. General corrosion is the only form of corrosion for which weight loss data can be used to estimate penetration rates accurately. General corrosion of copper alloys result from prolonged contact with environments in which the corrosion rate is very slow, such as fresh, brackish, and salt waters, many types of soils, neutral, alkaline, and acid solutions, and organic acids [5]. Other substances that cause uniform thinning, but at a faster rate, include oxidizing acids, sulfur-bearing compounds, NH₃, and cyanides [5]. In the repository environment being considered, this form of corrosion of the HLW canisters is unlikely to be the dominant mode of failure, and is therefore of not much interest.

Pitting Corrosion. As with most commercial metals, corrosion of copper metals results in pitting under certain conditions. Pitting is sometimes general over the entire surface, giving the metal an irregular and roughened appearance. In other cases, pits are concentrated in specific areas and are of various sizes and shapes. Pitting is the usual form of corrosion attack on surfaces which have incomplete protective films, nonprotective deposits of scale, or extraneous deposits of dirt or other foreign substances [5]. In the localized form of pitting the corroded product loses its load-carrying capacity and increases stress concentration by creating depressions or holes in the metal. The occurrence of pitting is somewhat random regarding the specific location

of a pit on the surface as well as whether it will even occur on a particular metal sample. Long-term tests of copper alloys show that the average pit depth does not continually increase with extended times of exposure (like in some stainless steels when exposed to chloride containing environments). Instead, pits tend to reach a certain limit beyond which little apparent increase in depth occurs [5].

Copper alloys do not corrode primarily by pitting, but because of metallurgical and environmental factors that are not completely understood, the corroded surface does show a tendency towards nonuniformity [5].

Pitting of copper in fresh water can be classified into two major types [13]. Type 1 pitting is usually associated with certain hard or moderately hard waters. It is more likely to occur in cold water than in hot water and may cause perforation in domestic plumbing in only one or two years. It is characterized by the formation of fairly large well-defined pits usually containing soft crystalline cuprous oxide (and often cuprous chloride) beneath hard mounds of calcium carbonate or basic copper carbonate. Fig. 3 shows schematically a pit formed on a copper surface in hard water [13]. Type 2 pitting occurs only in certain soft waters and is practically unknown at water temperatures below 60°C. It is characterized by deep pits of small cross section containing very hard crystalline cuprous oxide and capped by small black or greenish mounds of cuprous oxide or basic copper sulfate.

Of the copper alloys, the most pit resistant are the aluminum bronzes with less than 8% aluminum and low-zinc brasses [5]. Cupro-nickel alloys tend to have intermediate pitting resistance, but copper and high-copper alloys are somewhat more prone to pitting [5]. Based on the available information about the likely water chemistry to be found in the Yucca Mountain repository, one could expect Type 1 pitting after 1000+ years when the surface temperature of the canisters has dropped below 60°C [14].

Crevice Corrosion. This form of corrosion occurs near a crevice formed either by two metal surfaces or a metal and a nonmetal surface. Like pitting, crevice attack is a random occurrence, the precise location of which cannot always be predicted. Also, like pitting the depth of attack appears to level off rather than to increase continually with time. This depth is usually less than that from pitting, and for most copper-based alloys, it will be less than 400 μm [5]. The sites for this type of corrosion are unavoidable because of structural or functional design and may even arise during the exposure period. Examples of sites include spot-welded lap joints, threaded or riveted connections, presence of foreign objects or debris, such as dirt or even accumulation of corrosion products on the metallic surface. This type of attack can sometimes be controlled by cleaning the surface. For example, condensers & heat exchangers are cleaned periodically to prevent deposit attack [5]. Such a cleaning process, obviously, is not possible for the HLW canisters after emplacement in the deep geological repository.

The mechanism of crevice corrosion has been attributed to either differential aeration or metal-ion concentration cells [11]. It has been

suggested that more noble potentials support crevice attack whereas more active potentials favor repassivation within the crevice by a second protective film. Since this crevice protection potential is dependent on the nature of the potential-pH diagram for copper, it has been suggested that this concept might be applicable to all copper-based alloys having the same general features in their potential-pH diagrams [15]. Aluminum and chromium bearing copper-based alloys, which form passive surface films, are susceptible to differential oxygen cell attack, as are aluminum alloys and stainless steels [5].

For most copper alloys the location of the attack will be outside but immediately adjacent to the crevice due to the formation of metal ion concentration cells. Classic crevice corrosion resulting from oxygen depletion & attack within the crevice is less common in copper alloys. The occurrences of crevice attack is somewhat statistical in nature, with the odds of it occurring and its severity increasing if the area within a crevice is small compared to the area outside the crevice. This kind of situation exists in the present reference design for the HLW waste canister, where the waste canister is placed on a bottom support plate [4]. Other conditions that will increase the odds of crevice attack are higher water temperatures or a flow condition on the surface outside the crevice [5]. Based on the literature information, alloy CDA715 is expected to generally show the best crevice corrosion resistance, followed by alloy CDA613. Of the three materials being considered alloy CDA102 is reported to be most likely to be susceptible to crevice corrosion [14]. Since the temperature of the canister containing spent fuel is expected to be higher than canister containing vitrified waste, at all times during the first several thousands years, and assuming the water intrusion in the repository will occur when the spent fuel canister temperature drops below the boiling point of water, one would expect the spent fuel containing canisters to exhibit a higher degree of crevice corrosion attack.

Stress Corrosion Cracking (SCC). Stress Corrosion Cracking (SCC) and season cracking describe the same phenomena-- the apparently spontaneous cracking of stressed metal [6,15]. A specific corrosion environment and sustained stress are the primary causes of SCC; microstructure and alloy composition may affect the rate of crack propagation in susceptible alloys. Stress corrosion cracking is often intergranular(IGSCC), but transgranular(TGSCC) cracking may occur in some copper-based alloys in certain environments [5].

Applied and residual stresses can both lead to failure by SCC. Susceptibility is largely a function of stress magnitude. Stresses near the yield strength are usually required, but parts have failed under much lower stresses. In general, the higher the stress, the weaker the corroding medium must be to cause SCC. The reverse is also true: the stronger the corroding medium, the lower the required stress. Applied stress, in HLW canisters, can result from ordinary service loading or from fabrication processes, such as shrink fitting, bolting, riveting, brazing, or welding.

All copper-based alloys can be made to crack in NH_3 vapor, NH_3 solutions, ammonium ions (NH_4^+) solutions, and environments in which NH_3

is a reaction product. The rate at which cracks develop is critically dependent on many variables, including stress level, specific alloy, oxygen concentration in the liquid, pH, NH_3 or NH_4 concentration, copper ions concentration, etc. For copper alloys, generally, both oxygen and moisture must be present for NH_3 to be corrosive [5]. Other compounds, such as CO_2 , are thought to accelerate SCC in NH_3 atmospheres. Moisture films on metal surfaces will dissolve significant quantities of NH_3 , even from atmospheres with low NH_3 concentrations and can result in concentrations that could lead to SCC [5].

One scenario for generation of SCC promoting chemical species on the surface of a HLW canister is gamma radiolysis. For example, acidic nitrite could be generated in this manner, which could possibly lead to SCC. Fig. 4 [17] shows the dependence of the failure stress on nitrite concentration. The specimens in this case were strained at $2.6 \times 10^{-6} \text{ s}^{-1}$ while being maintained at 25°C and 100 mV, SCE.

Of the three HLW canister candidate materials, alloy CDA102 has been observed to fail in IGSCC mode in non-tarnishing ammoniacal solutions and cupric acetate solutions. TGSCC of CDA102 is observed in tarnishing ammoniacal and ammonium hydroxide solutions and nitrite solutions. Both film rupture [18] and film-induced cleavage [19] have been used to explain SCC of pure copper and alpha brasses. The tarnish film involved in the SCC of copper is believed to be Cu_2O [14]. Growth of this oxide obeys the parabolic law, which is consistent with the film-rupture model as well as the slip dissolution-repassivation model [20]. Copper deoxidized with phosphorus (CDA122) is prone to both embrittlement and IGSCC. (This grade is not being considered for the HLW canister). Copper-phosphorous alloys are most susceptible to IGSCC at approximately 0.2% phosphorous content [21,22].

Aluminum bronzes (similar to CDA613) have been reported to exhibit TGSCC in moist ammonia-containing environments [5]. In certain environments, corrosion can lower the fatigue limit to 25 to 59% of the normal atmospheric value [5]. Aluminum bronzes with aluminum content intermediate to those of CDA102 and CDA613 (approx. 1% aluminum) is more susceptible to SCC than aluminum bronzes of other compositions [21,22]. IGSCC of aluminum bronzes is known to occur in steam environments, probably because of the formation of Al_2O_3 at grain boundaries, but it can be effectively inhibited by small additions of aluminum.

IGSCC of cupro-nickel alloys, such as CDA715, may occur in steam environments, but these alloys are much less susceptible to IGSCC than aluminum bronzes (without tin inhibitor). TGSCC of cupro-nickel alloys may occur in moist ammonia containing environments, but these alloys are reported to be much less susceptible to TGSCC than aluminum bronzes (such as CDA613). The passive films on cupro-nickel alloys is believed to be $\text{Ni}(\text{OH})_2$. Based on the literature information, it appears that alloys CDA715 and CDA102 may provide better resistance to SCC in aggressive environments than CDA102.

Dealloying (Selective Leaching). Dealloying is a corrosion process in which the more active metal (less noble) is selectively leached (removed) from an alloy, leaving behind a weak spongy structure

of more noble metal. Unless arrested, dealloying eventually affects the entire bulk of the metal, weakening it structurally and allowing the contents (liquids or gases) to be released through the porous mass in the remaining structure.

There are two types of commonly recognized dealloying, the plug-type refers to dealloying that occurs in local areas, while the surrounding areas usually are unaffected or only slightly corroded. In the second type, layer- or delamination-type, the active component of the alloy leaches over a broad area of the surface. There is no standard method for evaluating the dealloying corrosion, but the phenomena is quite often characterized by visual changes in the color of the specimen, weight loss of the specimen, and chemical composition changes on the surface.

One mechanism considered for dealloying is the selective dissolution of one metal leaving behind a residual mass of the other metal. Another, more commonly accepted, mechanism involves the simultaneous dissolution of both principal alloying elements followed by a subsequent redeposition or precipitation of one alloying element (usually the major constituent) at favorable sites. Some observers conclude that both mechanisms exist, depending on various external influences, or that selective removal of one constituent may serve as a starting mechanism creating favorable sites for the subsequent deposition of one of the elements after the alloy dissolves as an entity. Although there has been controversy concerning the validity of the two mechanisms for many years, neither appears to adequately explain all observations so far reported, and no other truly different explanation of dealloying has been offered.

Dealloying of aluminum occurs in copper-aluminum alloys, particularly with those having more than 8% aluminum (aluminum bronzes). It is especially severe in alloys with continuous gamma-phase and usually occurs as plug-type dealloying. No effective minor alloying additions have been found for aluminum bronzes, but heat treatment offers some success in limiting delamination-type dealloying. Dealloying of nickel in copper-nickel alloys, although rare, has been observed at temperatures over 100°C, low flow conditions, and high local heat flux; conditions that can occur in the Yucca Mountain repository environment.

Based on the literature information, there is a possibility of dealloying (selective leaching) in both aluminum-bronze (CDA613) and cupro-nickel (CDA715) upon intrusion of water in the repository. The rate of dealloying attack is usually quite high, therefore damage to the HLW waste canisters could be expected in rather short duration of time as compared to other degradation mechanisms.

Galvanic Corrosion. When two dissimilar metals are in electrical contact with each other and immersed in a conductive solution, a potential results that enhances the corrosion of the more negative member of the couple (the anode) and partly or completely protects the more electropositive member (the cathode). Fig. 5 [5] lists a galvanic series of metals and alloys valid for dilute aqueous solutions, such as

seawater and weak acids. The metals that are grouped together can be coupled to each other without significant galvanic damage. However, the connecting of metals from different groups leads to damage of the more anodic metal. The larger the difference in galvanic potential between groups, the greater the corrosion [5].

Copper and its alloys are almost always cathodic to other common structural metals, such as carbon steel and aluminum. When carbon steel or aluminum is put in contact with copper or a copper-based alloy, the corrosion rate of the steel or aluminum increases, but that of the copper metal decreases. However, it is reported in literature that common grades of stainless steel exhibit variable behavior depending on conditions of exposure [5]. Copper alloys are reported to corrode preferentially when coupled with high-nickel alloys, titanium, or graphite. This degradation mechanism, i.e. galvanic corrosion, will be of concern if incompatible alloys are used in the repository. According to the present plans, the pour canister (inside canister) containing vitrified waste will be fabricated from Type 304L stainless steel. Although, there is little likelihood of any galvanic corrosion cell to be set-up between the outer copper-based alloy canister and the pour canister as long as the outside canister is intact, a scenario with a small pinhole type breach of the outer canister could let some liquids in in the outer canister leading to galvanic corrosion attack.

Another important factor that affects galvanic corrosion is area ratio. An unfavorable area ratio exists when cathodic area is large and the anodic area is small. The corrosion rate of the small anodic area may be several hundred times greater than if the anodic and cathodic areas were equal in size. Conversely, when a large anodic area is coupled to a small cathodic area, current density and damage due to galvanic corrosion are much less [5]. In the case of the HLW canisters containing vitrified waste, the pour canister (stainless steel) area would be much smaller than the outer copper-based alloy canister creating an unfavorable situation which could accelerate the degradation of the inside pour canister. While the situation in the case of the HLW canisters containing spent fuel (clad in zirconium-based alloy cladding) would be the opposite. Only a limited number of galvanic corrosion studies related to HLW canister materials are reported in the literature. In one such study, it is reported that no galvanic corrosion was observed between copper and Zircaloy fuel cladding containing spent fuel [23]. However, the test duration was very short and the number of test samples were too few to draw definitive conclusions.

VARIABLES WITH SIGNIFICANT AFFECT ON THE CORROSION RATES (Affect of Oxygen, pH, Temperature, Chloride, and Sulfides)

Oxygen, which is one of the most important factors in aqueous corrosion of copper-based alloys, oxidizes cuprous ions to more corrosive cupric state, thus promoting the formation of a protective film [24]. In high temperature seawater, acceptable low corrosion rates are only observed under low oxygen (deaerated) conditions as shown in Fig. 6 [25]. Also, results from tests in desalting environments indicate

that useful high-temperature service of copper alloys in desalting plants can only be assured if oxygen content is kept low [24]. The reduction in corrosion rates observed with increasing temperature is probably a result of the reduced oxygen solubility in water at higher temperature. In the presence of oxygen, increasing temperature increases the corrosion rate of copper-based alloys [11].

The influence of pH is obvious from the potential-pH diagram shown in Fig. 2 [11]. In acidic solutions, the controlling cathodic reaction is one of oxygen reduction according to reaction to the following reaction [11].



Low pH prevents copper-base alloys from developing protective films, resulting in high corrosion rates. High oxygen levels, in combination with low pH, further accelerate corrosion. Chloride tends to promote localized forms of corrosion. Dealloying (particularly in aluminum bronzes) are more likely to occur in warm or hot waters with relatively high chloride concentrations. Such a situation, leading to concentration of chloride ions, is possible in a repository if the waters were to intrude the repository in waves, i.e. intrusion followed by evaporation and then refluxing. A high $SO_4^{2-}:Cl^-$ ratio favors pitting in copper alloys [26], which is opposite to the conditions which favor pitting attack in stainless steels. Chloride, in combination with free carbon dioxide, sulfate and high temperature, also promote high dissolution rates in aqueous media. The formation of carbonic acid, even though weak, prevents the formation of protective films ordinarily developed on copper [27].

Water becomes very aggressive to copper and its alloys when contaminated with sulfides [28-32]. In sulfide containing waters, a copper sulfide film is formed on the surface which is more cathodic than the corrosion film developed in pure waters. Breaks in the sulfide film greatly stimulate local attack by pitting because of the large cathodic area. Sulfide concentrations as low as 0.1 mg/L have been reported to have caused accelerated attack on copper alloys [29], and vigorous attack has been observed on cupro-nickel alloys at sulfide concentrations of 0.2 mg/L in sea water. Maximum pit depths of 0.5 mm have been observed within 15 days exposure. The effects of oxygen on sulfides are synergistic and combinations of 0.06 mg/L sulfide and 0.8 mg/L O_2 can increase normal corrosion rates in pure water by a factor of 10 [30].

DEGRADATION OF COPPER-BASED ALLOYS UNDER RADIATION

One feature of the Yucca Mountain, Nevada, HLW repository will be the initial presence of ionizing gamma radiation at high dose rates. The interaction of gamma radiation with aqueous environment is expected to produce a host of transient radicals, ions and molecular species,

including hydrogen peroxide. In the moist air phase, nitric acid and various oxides of nitrogen are expected to form which may dissolve in the liquid water phase present. These radiation induced changes in the chemical environment of the copper-based alloy canister could be expected to alter mechanisms of corrosion and/or normal rates observed for the same mechanisms without the gamma radiation.

Since materials degradation/corrosion data obtain in non radiation environment is not easily extrapolatable to radiation environments, there is a need to conduct tests in simulated repository environments including the radiation field. Only a limited number of tests have been reported under such conditions. The results of these tests are reported and discussed in this section.

Test Conditions. The three candidate HLW canister alloys are reported to have been tested under simulated Yucca Mountain repository environment to identify the degradation mechanisms and plan future tests in the areas of most concern [33]. The three types of environment that are likely to exist in the repository over the long period of interest, spanning thousands of years, were simulated in autoclave tests by exposing the test materials to air-water vapor mixture at 150°C (representing early years in the unsaturated zone in the repository), to water-vapor saturated air phase above liquid water at 95°C (representing middle years of the canister service conditions in the repository), and by immersing in the liquid water phase at 95°C (representing the later part of the life in the repository). The water used for the experiments was from well No. J-13 on the Nevada Test Site near the Yucca Mountain [33]. The radiation field to which the test specimens were exposed was approx. 1×10^5 rad/h, with exposure times ranging from 1 to 14 months. The test data obtained included visual examination for evidence of localized attack (pitting, crevice corrosion, stress corrosion cracking), weight loss measurements (for estimating general corrosion rates), and chemical compositions of the surface films (for identifying migration profiles of alloying elements and to determine the stoichiometry of the surface oxide films) [7,33,34].

Summary of the Test Results. The significant results of the experimental investigations can be summarized, in quantitative terms, as follows:

- . all three copper-based HLW canister alloys are susceptible to pitting
- . alloy CDA 613 exhibited filiform-like (underfilm) corrosion, generally observed only in aluminum alloys, which has not been reported earlier in the literature on CDA613.
- . none of the three alloys exhibited stress corrosion cracking (SCC)

- . crevice corrosion was observed on all test samples representing all three alloys. However, it appeared to be a function of crevice geometry. Tight crevices being immune to accelerated crevice corrosion.
- . CDA613 showed a distinct layer enriched in aluminum, positioned between the outer surface of the oxide & the base metal
- . CDA715 showed a layer high in nickel content over a layer relatively high in copper content
- . most severe corrosion appeared to be related to the presence of small amounts of liquid water on the metal surface, either in films or drops
- . the "uniform" corrosion rates measured without gamma radiation were comparable to the corrosion data under radiation for CDA101 and CDA613 [7,33,34]. However, the rates were much higher for alloy CDA715 under saturated vapor conditions in the presence of gamma-radiation.
- . based on the weight loss measurements from approx. 5,000 h exposures, the "uniform" corrosion rates for the three alloys tested range from a minimum of 0.30 $\mu\text{m}/\text{y}$ for CDA613 to a maximum of 5.6 $\mu\text{m}/\text{y}$ for CDA715
- . the most uniform corrosion surfaces were observed on CDA101, and the least uniform (with obvious spalling) on CDA715.
- . pitting on CDA101 alloy coupons appeared to be associated with foreign particles and materials that were embedded in the specimen surface during fabrication.
- . corrosion rate of alloy CDA101 was in between those of CDA613 and CDA715
- . stoichiometries observed in the oxide layers of alloy CDA101 seem to be Cu_2O in the oxide produced in the gas phase, and closer to CuO for those produced in the liquid phase. On the CDA715 and CDA613 alloys only CuO phase was detected.
- . copper-colored phases are clearly visible near many of the pits, in all three copper-based alloys tested
- . from the corrosion pattern found in the welds of the tear drop specimens, it appeared that there may be some enrichment of component metals during the process of fusion welding of alloy CDA613.
- . CDA715 alloy exhibited severe roughening of the metal surfaces under the oxide layer in corrosion tests conducted in the saturated vapor phase at 95°C. [The corrosion rate of CDA715 was the highest in this environment]

- . the oxide films on alloy CDA715 were dark and thick and show a tendency to spall, leaving small craters in the oxide layer
- . the crevice corrosion (around the support ceramic washers) was the most severe in CDA715 compared to the other two test materials

Discussion of Quantitative Data. The reported [7,33,34] coupon weight loss data and calculated "uniform" corrosion rates in mil/y, for the three corrosion environments mentioned earlier, are shown in Fig. 7 and 8. The bar chart in Fig. 9 shows the "uniform" corrosion rate data plotted for easy comparison. The data in these three plots were obtained under gamma radiation dose rate of approx. 1×10^5 rad/h. The trend that are obvious from these 3 figures is that 95°C saturated steam environment is the most aggressive of the three test environments for all three copper-based alloys, while the 150°C unsaturated steam phase is the least aggressive. The samples immersed in water at 95°C exhibit intermediate corrosion rates.

Test data obtained on the three HLW candidate canister alloys under similar three environments but without the radiation [34] are shown in the bar charts in Fig. 10. Comparison of the test data for irradiated samples with non-irradiated samples show similar corrosion trends in the three environments for CDA101/102 and CDA613/614, while the alloy CDA715 shows water to be the most aggressive environment followed by saturated steam at 100°C; the 150°C unsaturated steam environment was found to be the least aggressive.

Comparison of the data for irradiated versus non-irradiated samples for the three tests alloys are shown in bar charts in Figs. 11, 12, and 13, indicating that in all three environments (steam at 150°C, steam at 95°C/100°C, and water at 95°C/100°C), the gamma-radiation changes the corrosion rates slightly for CDA 101/102 and CDA 613/614, whereas there is a dramatic increase in the corrosion rate of alloy CDA715 in 95°C saturated steam environment. Figure 14 shows the same comparative data as in bar charts in Fig. 11, 12, and 13, condensed into one figure. Careful observation of the data in Fig. 14 indicates the corrosion rates for CDA715 to be lower in 100°C saturated steam than in water at 100°C, which is opposite of the trend in the two other materials, viz. CDA101 and CDA613. The questions that comes to the mind are: (i) Is this related to experimental errors and limited number of test samples used or is this a trend? and (ii) if this is a trend, is the mechanism of oxide film growth in alloy CDA715 different/more sensitive to the environment than the other two alloys (since all weight measurements in a way represent the kinetics of the surface oxide film growth)?

From the corrosion data presented, one would tend to rank alloy CDA613 as the best from "uniform" corrosion point of view under gamma-radiation, and CDA715 as the worst. However, if one looks at Fig. 8, it is clear that all corrosion rate curves have not levelled-off in all three environments (exceptions being the the curves for alloys CDA101 and CDA715 in 95°C saturated steam phase). From this figure one could infer that the corrosion rate kinetics (rate of growth of oxide film),

while exhibiting similarly reducing rate trend, are quite different in numerical values for the three alloys, and that it may be possible for the corrosion rates in alloys CDA715 and CDA101, in 95°C steam phase, to come down with additional exposure. On the other hand, it may, also, be possible that spallation, reported for alloy CDA715 [7,33,34], may increase the calculated "uniform" corrosion rate at longer exposures if the spalled regions do not grow equally passive films in a short time.

The papers/reports providing the corrosion data presented here do not provide any explanation of the spalling of the oxide film observed on alloy CDA715. One possible explanation, suggested here, could be that spallation of the oxide layer on CDA715 is related to the stress build up in the oxide layer (as a result of volume increase when metal oxidizes). If spallation of the oxide film is related purely to the mechanical stresses, as suggested here, then one may expect to see spallation in CDA613 when oxide thickness reaches the same dimensions as observed on CDA715 (since the stoichiometry of the oxide film is the same (CuO), and assuming the same metal-oxide interface bond strength for the two alloys). However, in the case of alloy CDA613 one may need much longer exposure time due to the slower kinetics of the oxide film growth. Similar argument can be made for alloy CDA101, but in this case based purely on the metal-oxide interface stress build up, one could expect the oxide film to spall off after reaching a much greater thickness than the other two alloys since the stoichiometry of the oxide on CDA101 is $Cu_2O + CuO$ (again this argument assumes same metal-oxide interface bond strength as the other two copper-based alloys). Since the test exposure time was too short, there is a feeling that we may still be in the transient state of the film build up. Until and unless will get into the steady state (or it is determined that there will never be a steady state, but only cycles of film growth followed by spallation), it is not possible to make any meaningful judgements about the film growth kinetics. ??

The results of the corrosion tests under radiation seem to point out the need to better understand the kinetics of the surface oxide film growth in the three candidate HLW canister materials. Some of the important questions that need to be answered are:

- . is the spallation observed in alloy CDA715 oxide film related to stress build-up at the metal-oxide interface (or at the location where the separation occurs)?
- . is the spallation in alloy CDA715 related to gamma-radiation? or radiolysis products?
- . what are the kinetics of the new oxide film that forms on the regions where the old film spalls-off? Is there a memory effect? (Do the kinetics of the new film formation follow corrosion kinetics of the old film at the time of spallation or of the film formation on a fresh metal surface?)
- . will the oxide films that form on the alloys CDA613 and CDA101 eventually spall-off due to stress build-up, as suggested here? What are the kinetics of the new oxide film that forms on the

regions where the old oxide film spalls-off?

since the most likely conditions in the repository (as presently assumed) are going to be high temperature (>150°C unsaturated steam coupled with ionizing radiation), followed by saturated steam at 95°C, followed by water at 95°C, and finally water at continually decreasing temperature, the film growth kinetics in constant environmental conditions may not provide all the data that might be essential to model the long-term degradation of the HLW canisters. Therefore, one needs to know the oxide film growth kinetics under varying environmental conditions, e.g. how will the ~~thin~~ thin oxide film (pre-film) generated under certain environment affect subsequent film build-up under a different environment (differing in temperature, phase of the water, chemical species, radiation level, etc.)

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CONCLUSION

Survey of the literature has indicated that all three candidate HLW copper-based alloys can be may made to "degrade" given long enough exposure in an appropriate environment. The three copper-based alloys being considered show quite different susceptibility to different environments, therefore the ranking of these alloys will change depending on how the different modes of degradation are weighted. The three degradation modes that can be considered important in the repository environment, requiring detailed mechanistic understanding, are: stress corrosion cracking, pitting, and crevice corrosion. Paucity of validating experimental data in repository environments makes the use of data generated under different environments/service conditions difficult. However, the literature provides some very valuable information about the ways of reducing the likelihood of the occurrence of some of the degradation modes in the repository environment. There is a clear need to understand the kinetics of the surface oxide film formation and rupture in the three candidate copper-based alloys under expected environments in the Yucca Mountain repository. As stated earlier, the process of selection of the material(s) for the HLW canisters, by necessity, has to be iterative in nature, and has to take into consideration the design of canister, its contents, the other components of the engineered barrier system, the service environment over the entire period of interest (including how it may change with time), and the mechanistic understanding and kinetics of the the degradation processes that might be applicable to the canister material.

REFERENCES

1. U. S. Nuclear Regulatory Commission, "Disposal of High Level Radioactive Wastes in Geological Repositories", Code of Federal Regulations, Title 10, Part 60, U. S. Government Printing Office, Washington, D. C., 1984.
2. A. Cohen and W. Stuart Lyman, "Properties of Copper and Copper

- Alloys Under Consideration for Nuclear Waste Containers", Copper Development Association, Inc., Report, June 18, 1986.
3. C. F. Acton and R. D. McCright, "Feasibility Assessment of Copper-Base Waste Package Container Materials in a Tuff Repository", Lawrence Livermore National Laboratory, Report No. UCID-20847, September 30, 1986.
 4. Site Characterization Plan (SCP), Yucca Mountain Site, Nevada Research and Development Area, U. S. Department of Energy, Report No. DOE/RW-0199, December 1988.
 5. Corrosion of Copper and Copper Alloys, By ASM Committee on Corrosion of Copper, Chairman: Ned W. Polan, in ASMI Metals Handbook on Corrosion, Ninth Edition, Vol. 13, 1987.
 6. N. B. Pilling and R. E. Bedworth, Journal of Institute of Metals, Vol. 29, 1923.
 7. R. D. McCright, "FY 1985 Status Report on Feasibility Assessment of Copper-Base Waste Package Container Materials in a Tuff Repository", Lawrence Livermore National Laboratory, Report No. UCID-20509, September 30, 1985.
 8. S. Sato and K. Nagata, Boskoku Gijutsu, Vol. 23, 1974.
 9. M. G. Fontana and N. D. Green, in CORROSION ENGINEERING, Second Edition, McGraw-Hill, 1978.
 10. Corrosion of Copper and Copper Alloys, By ASM Committee on Corrosion of Copper, Chairman: Ned W. Polan, in ASMI Metals Handbook on Corrosion, Ninth Edition, Vol. 13, 1987.
 11. K. Nuttall and V. F. Urbanic, "An Assessment of Materials for Nuclear Fuel Immobilization Containers", Atomic Energy of Canada Limited, Whiteshell Nuclear Research Establishment, Report No. AECL-660, September 1981.
 12. M. Pourbaix, "Atlas of Potential/pH Diagrams", Pergamon Press, Oxford, 1962.
 13. H. S. Campbell, "A Review: Pitting Corrosion of Copper and its Alloys", Second Edition, Reinhold Publishing Company, 1963.
 14. J. C. Farmer and R. D. McCright, "Localized Corrosion and Stress Corrosion Cracking of Candidate Materials for High-Level Radioactive Waste Disposal Containers in U.S: A Literature Review", Lawrence Livermore National Laboratory, Report No. UCRL-98756, November 4, 1988. Also, presented as a paper at the Materials Research Society Meeting, Berlin, Federal Republic of Germany, October 10-13, 1988.
 15. E. N. Pugh, J. V. Craig, and A. J. Sedriks, "The Stress-Corrosion Cracking of Copper, Silver, and Gold Alloys", in Proceedings of

the Conference on Fundamental Aspects of Stress Corrosion Cracking, Ohio State University, Columbus, Ohio, September 11-15, 1967.

16. K. D. Efird and E. D. Verink, "The Crevice Protection Potential for 90-10 Copper Nickel", Corrosion, Vol. 33, No. 9, 1977.
17. L. A. Benjamin, D. Hardie, R. N. Parkins, "Investigation of the Stress Corrosion Cracking of Pure Copper", Swedish Nuclear Fuel and Waste Management Company, Stockholm, Sweden, KBS Technical Report No. 83-06, 1983.
18. Y. Suzuki, Y. Hisamatsu, "Stress Corrosion Cracking of Pure Copper in Dilute Ammoniacal Solutions", Corrosion Science, Vol 21, No. 5, 1981.
19. A. Paskin, K. Sieradzki, D. K. Som, G. J. Dienes, "Environmentally Induced Crack Nucleation and Brittle Fracture", Acta Metallurgica, Vol. 30, 1982.
20. T. Nakayama, M. Takano, "Application of the Slip Dissolution-Repassivation Model for Stress Corrosion Cracking of AISI 304 Stainless Steel in Boiling 42% MgCl₂ Solution", Corrosion, Vol. 42, No. 1, 1986.
21. E. N. Pugh, J. V. Craig, W. G. Montague, "Factors Influencing the Path of Stress-Corrosion Cracking in Alpha-Phase Copper Alloys Exposed to Aqueous Ammonia Environments", Transactions of the ASM, Vol 61, 1968.
22. D. H. Thompson, A. W. Tracy, "Influence of Composition on the Stress-Corrosion Cracking of Some Copper-Base Alloys", Metals Transactions, February 1949.
23. H. D. Smith, "The Influence of Copper on Zircaloy Spent Fuel Cladding under a Potential Tuff Repository Condition", Westinghouse Hanford Company, Report No. HEDL-SA-3583, UCRL-15993, DE88-004366, 1987. Also, presented at the Waste Management '87 Conference, Tucson, Arizona, March 1-5, 1987.
24. C. F. Schrieber and F. H. Coley, "Behavior of Metals in Desalting Environments: Seventh Progress Report (Summary)", Paper presented at NACE, Paper No. 36, Corrosion/75, Toronto, Canada, 1975.
25. W. K. Boyd and F. W. Fink, "Corrosion of Metals in Marine Environments", Metals and Ceramics Information Center, Battelle Columbus Laboratories, Report No. MCIC-75-245R, 1975.
26. L. L. Shreir, Corrosion, Vol. 1, Second Edition, Newnes-Butterworth, 1976.
27. J. M. Scluter, "Copper Alloy Tube Failures in Sea Water Condensers (Case History)", Materials Performance, Vol. 17, No. 2, 1978.

28. H. P. Hack and J. P. Gudas, "Inhibition of Sulfide-Induced Corrosion of Copper-Nickel Alloys with Ferrous Sulfate", *Materials Performance*, Vol. 18, No. 3, 1979.
29. J. P. Gudas and H. P. Hack, "Sulfide Induced Corrosion of Copper Nickel Alloys", *Corrosion*, Vol 35, No. 2, 1979.
30. B. C. Syrett, "Accelerated Corrosion of Copper in Flowing Pure Water Contaminated with Oxygen and Sulfide", *Corrosion*, Vol. 33, No. 7, 1977.
31. D. C. Vreeland, "Review of Corrosion Experience with Copper-Nickel Alloys in Sea Water Piping Systems", *Materials Performance*, Vol. 15, No. 10, 1976.
32. T. J. Lennox, M. H. Peterson and R. E. Groover, "De-Alloying of Copper Alloys and Response to Cathodic Protection in Quiescent Sea Water", *Materials Protection and Performance*, Vol. 10, No. 7, 1971.
33. W. H. Yunker and R. S. Glass, "Long-Term Corrosion Behavior of Copper-Base Materials in a Gamma-Irradiated Environment", Lawrence Livermore National Laboratory, Report No. UCRL-94500, DE87-007098, December 1986. Also, published in the Proceedings of the Materials Research Symposium L on Scientific Basis for Nuclear Waste Management, Boston, Mass., December 1-5, 1986.
34. W. H. Yunker, "Corrosion of Copper-Based Materials in Gamma Radiation", Westinghouse Hanford Company, Report No. HEDL-7612, DE87-005594, June 1986.

Copper or Copper Alloy	Composition, percent maximum (unless shown as a range or minimum)									
	Cu (incl. Ag)	Pb	Fe	Sn	Zn	Al	Mn	Si	Ni (incl. Co)	P
CDA 102	99.95 min.	--	--	--	--	--	--	--	--	--
CDA 613	Remainder	.01	2.0-3.0	.20-.50	.10 ^a	6.0-7.5	.20	.10	.15	.015
CDA 715	Remainder	.05 ^b	.40-1.0	--	1.0 ^b	--	1.0	--	29.0-33.0	--

^a When the product is for subsequent welding applications and is so specified by the purchaser, Cr, Cd, Zr and Zn shall each be .05 percent maximum.

^b When the product is for subsequent welding applications and is so specified by the purchaser, Zn shall be .50 percent maximum, P .02 percent maximum, Pb .02 percent maximum, S .02 percent maximum, and C .05 percent maximum.

Fig. 1. Composition of Candidate Copper-Based Alloys [4]

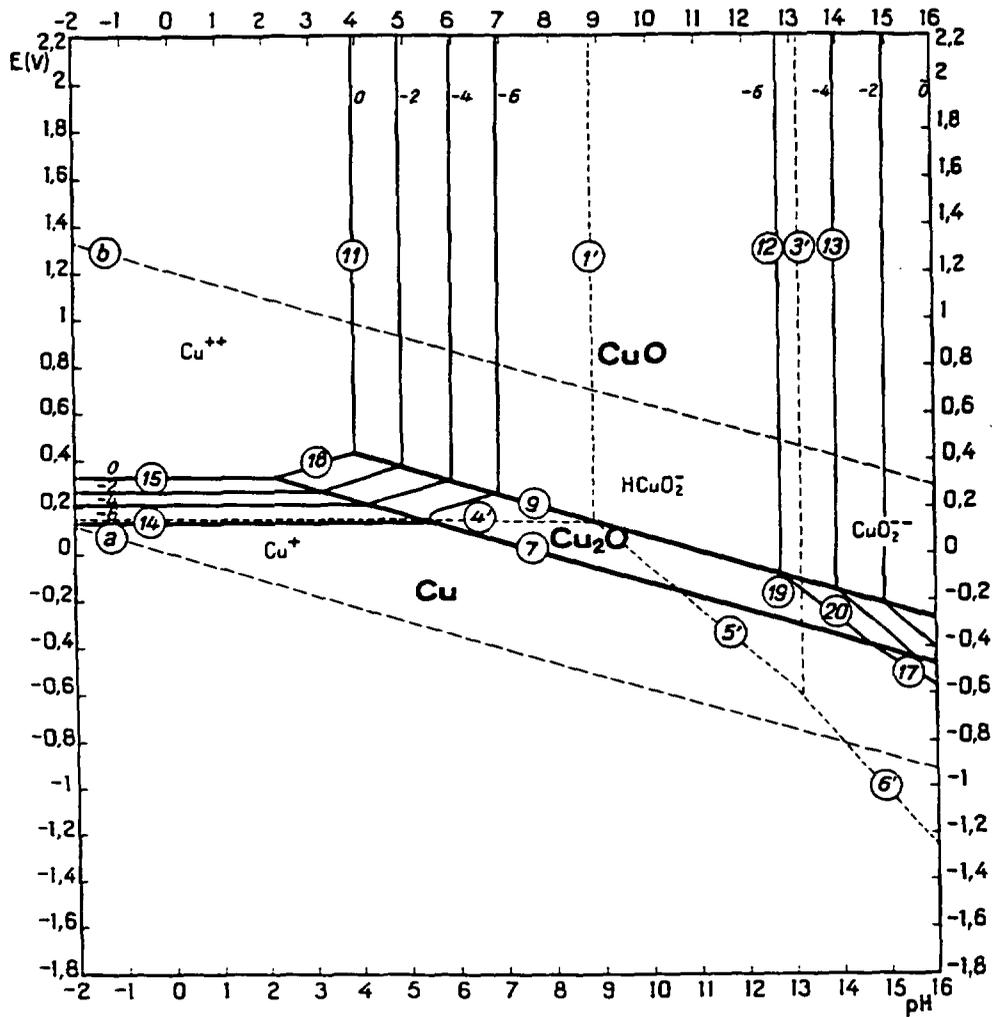


Fig. 2. Potential-pH Equilibrium Diagram for the System Copper-Water at 25°C [12]

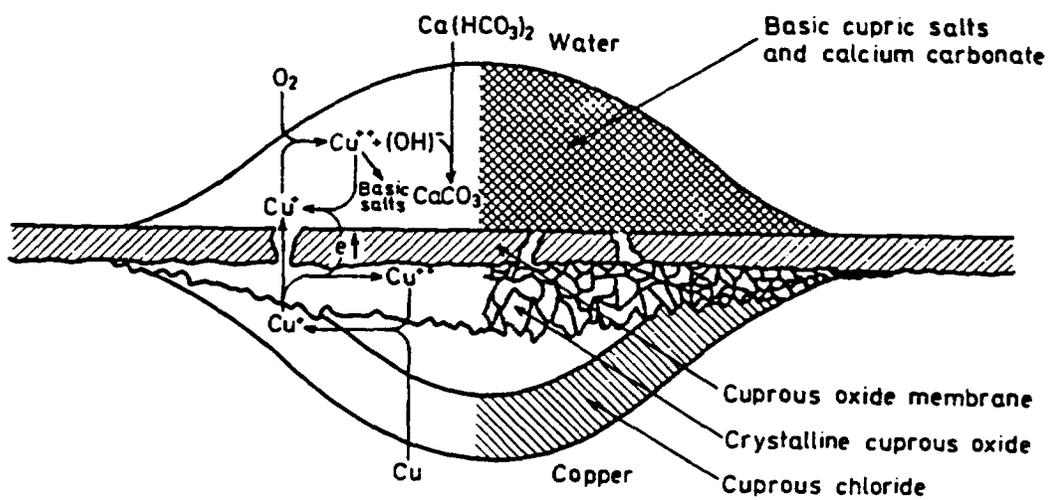


Fig. 3. Schematic of a Pit Formed on a Copper Surface
(Protected by a Film of Cu_2O) in a Hard Water [13]

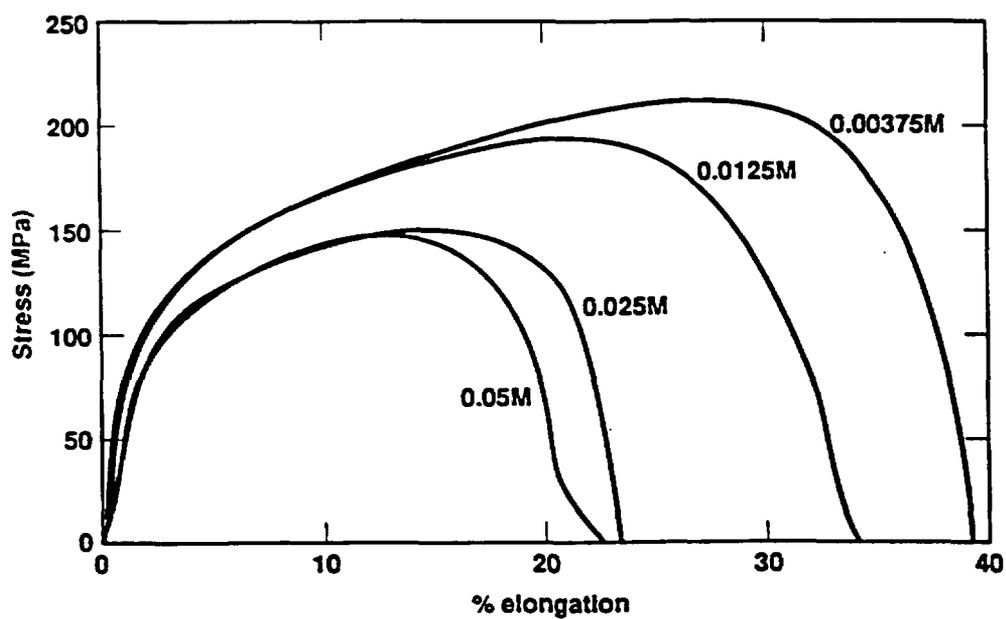


Fig. 4. Stress-elongation Curves from Slow Strain Tests of Oxygen-free Copper in Aerated Solutions of NaNO₂ at the Concentrations Shown. Room Temperature and an electrode potential of +100mV (SCE), Strain Rate of $2.6 \times 10^{-6} \text{ s}^{-1}$ [17]

Anodic End

Magnesium
Magnesium alloys
Zinc
Galvanized steel
Aluminum alloy 5052H
Aluminum alloy 3004
Aluminum alloy 3003
Aluminum alloy 1100
Aluminum alloy 6053
Alclad aluminum alloys
Cadmium
Aluminum alloy 2017
Aluminum alloy 2024
Low-carbon steel
Wrought iron
Cast iron
Ni-resist cast iron
AISI type 410 stainless steel (active)
50Pb-50Sn solder
AISI type 304 stainless steel (active)
AISI type 316 stainless steel (active)
Lead
Tin
Muntz metal (C28000)
Manganese bronze (C67500)
Naval brass (C46400)
Nickel (active)
Inconel (active)
Cartridge brass (C26000)
Admiralty metal (C44300)
Aluminum bronze (C61400)
Red brass (C23000)
Copper (C11000)
Silicon bronze (C65100)
Copper-nickel, 30% (C71500)
Nickel (passive)
Inconel (passive)
Monel
AISI type 304 stainless steel (passive)
AISI type 316 stainless steel (passive)
Silver
Gold
Platinum

Cathodic End

Fig. 5. Galvanic Series in Seawater [6]

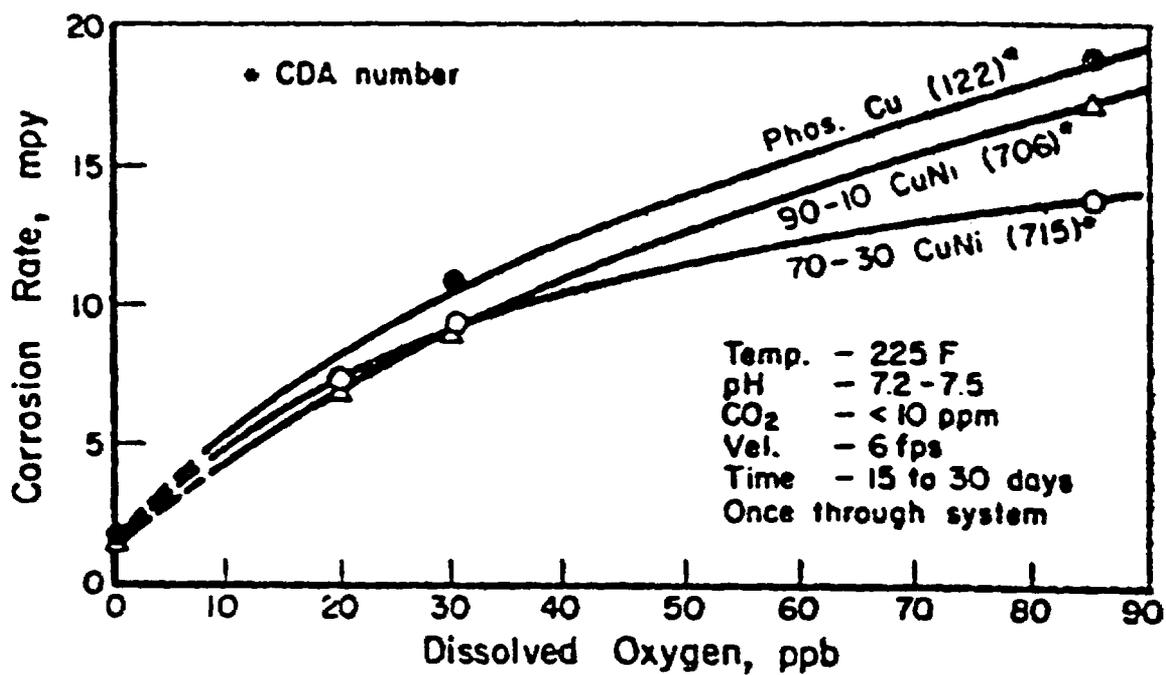


Fig. 6. Effect of Dissolved Oxygen in Seawater on the Corrosion Rate of Copper Alloys [25]

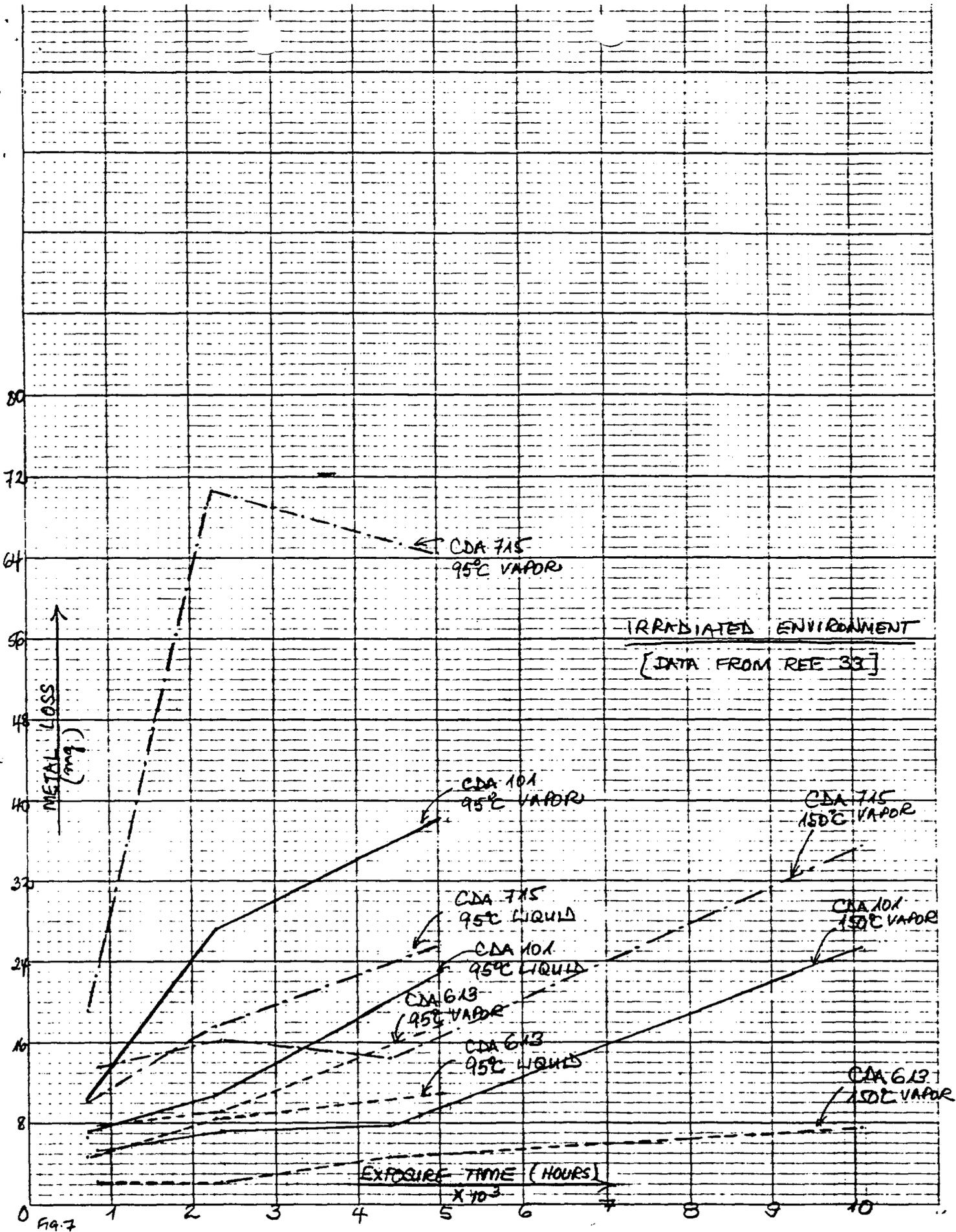


Fig. 7. Metal Loss As a Function of Environment and Exposure Time for Alloys CDA101, CDA613, and CDA715 (Irradiated Environments)

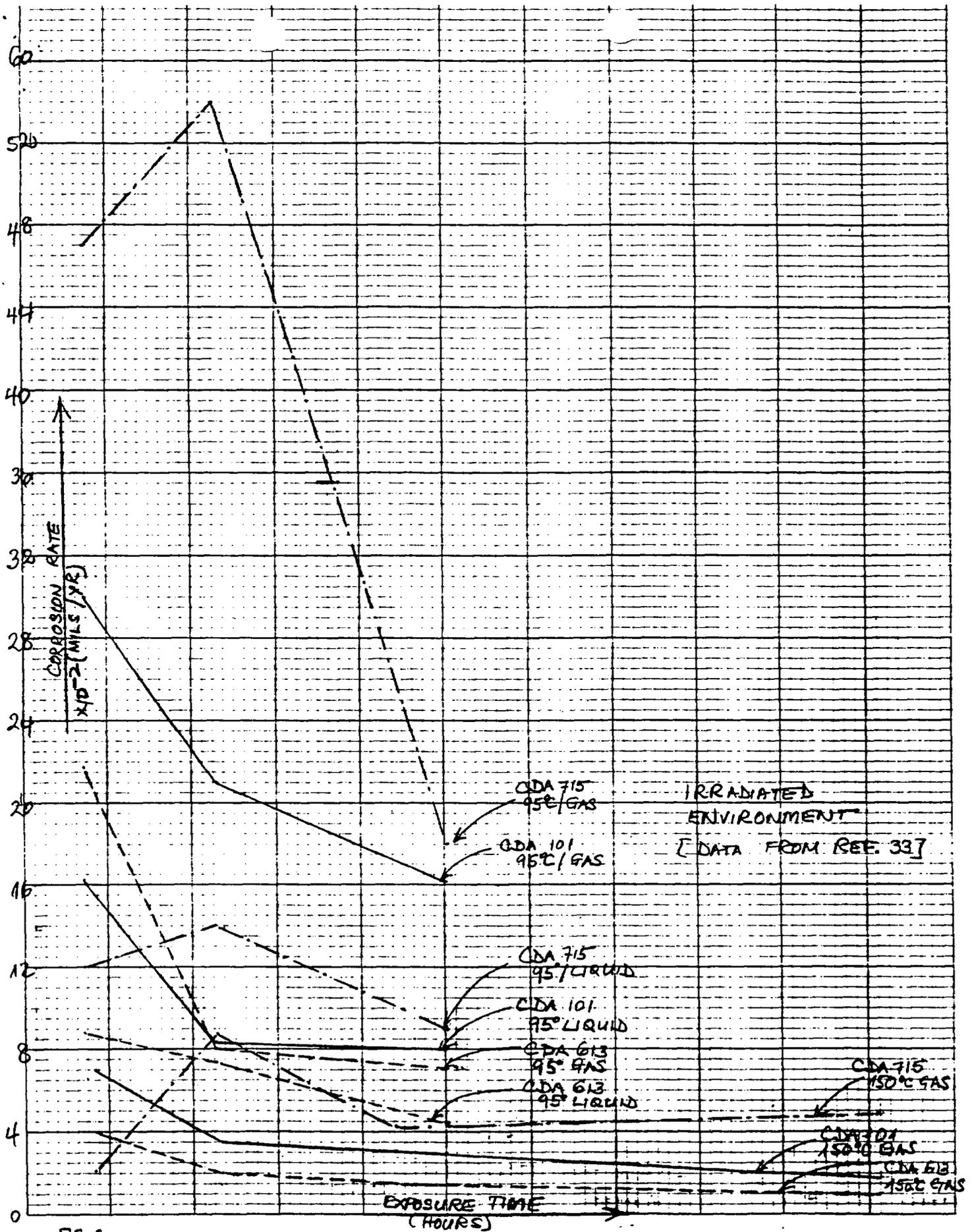


Fig. 8

Fig. 8. Corrosion Rates of Alloys CDA101, CDA613, and CDA715 as a Function of Environment (Irradiated Environments)

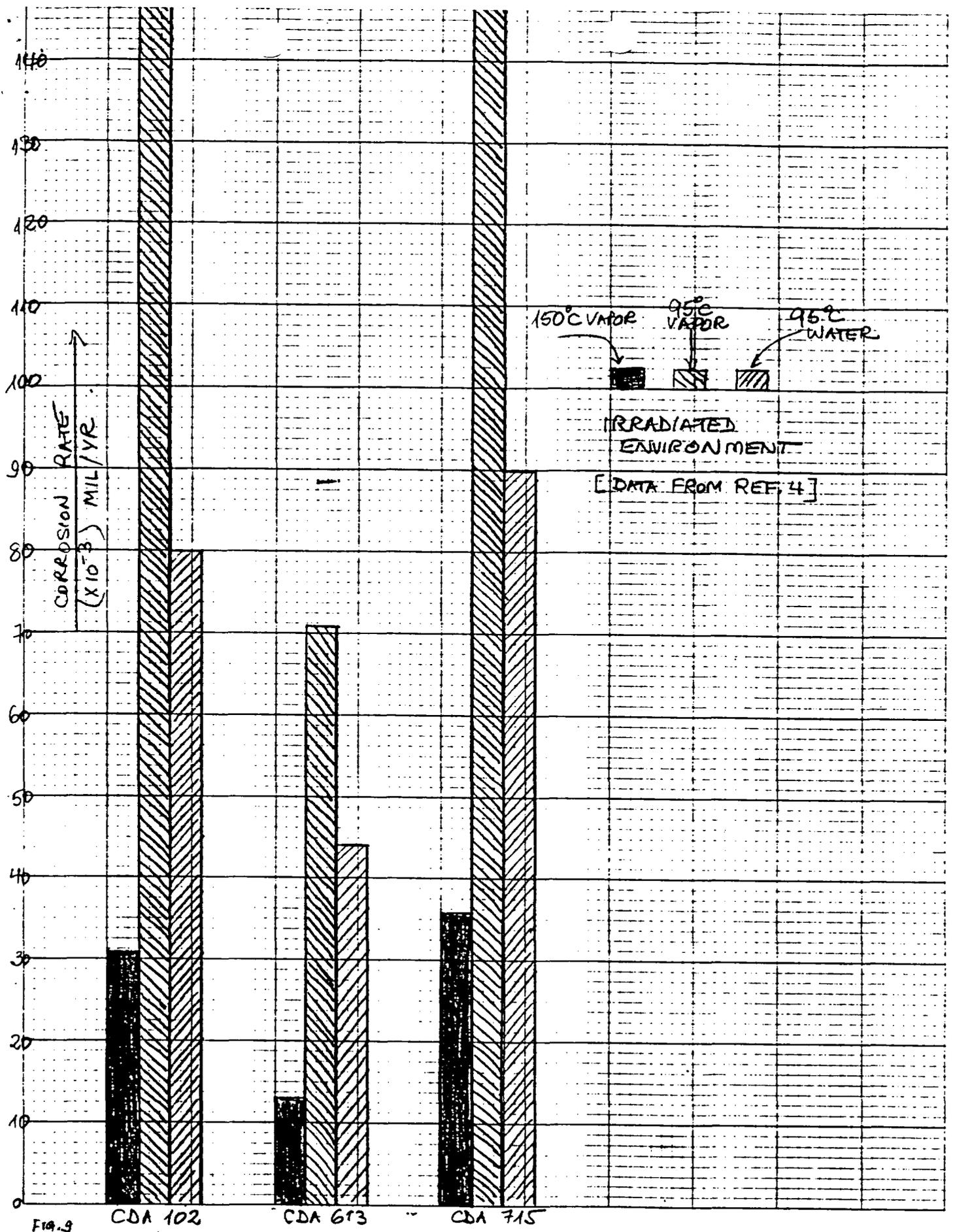


Fig. 9. Comparison of Corrosion Rates of Alloys CDA101, CDA613, and CDA715 as a Function of Environment (Irradiated Environments)

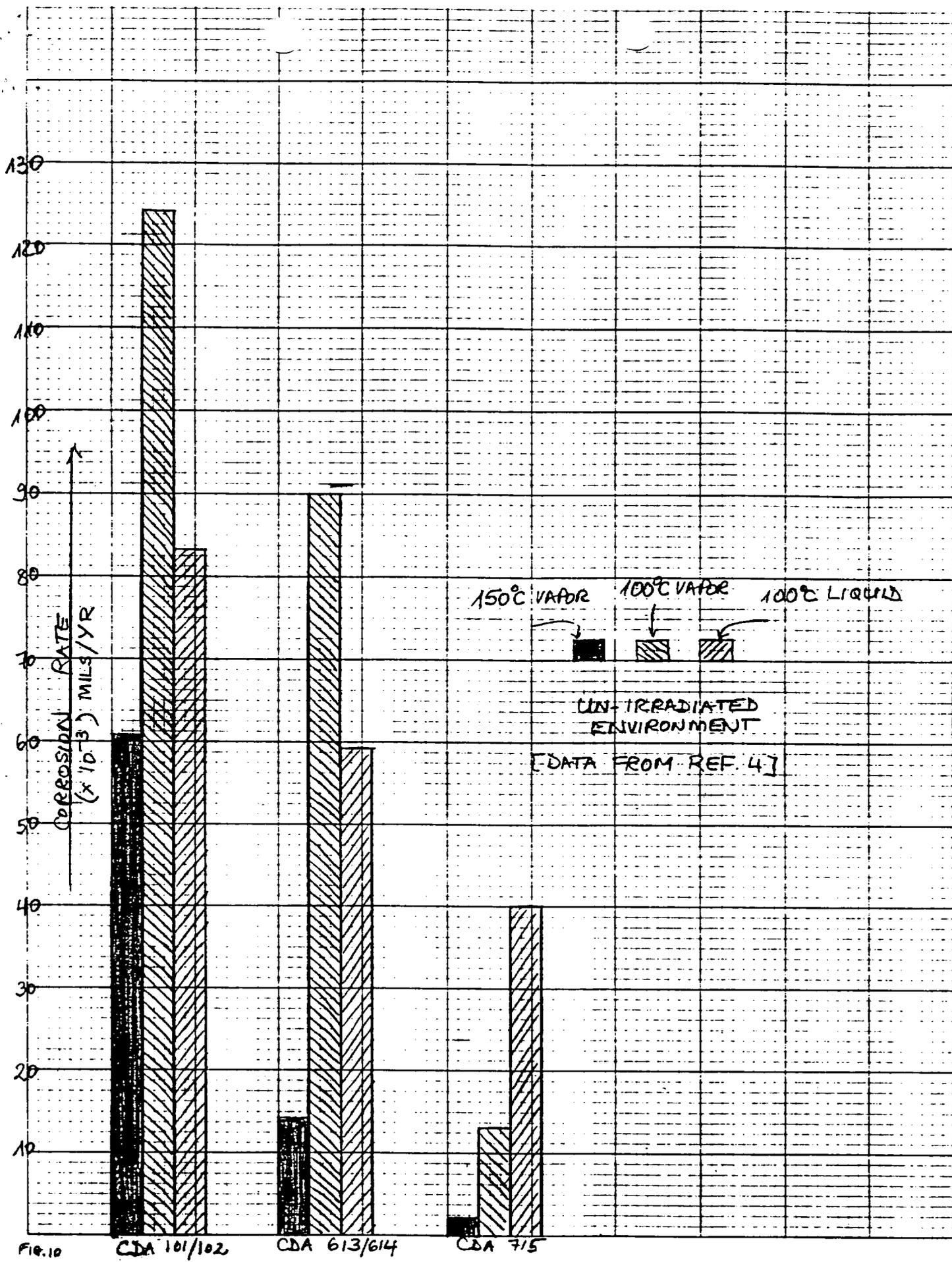


Fig. 10. Comparison of Corrosion Rates of Alloys CDA101/102, CDA613/614, and CDA715 as a Function of Environment (Un-irradiated Environments)

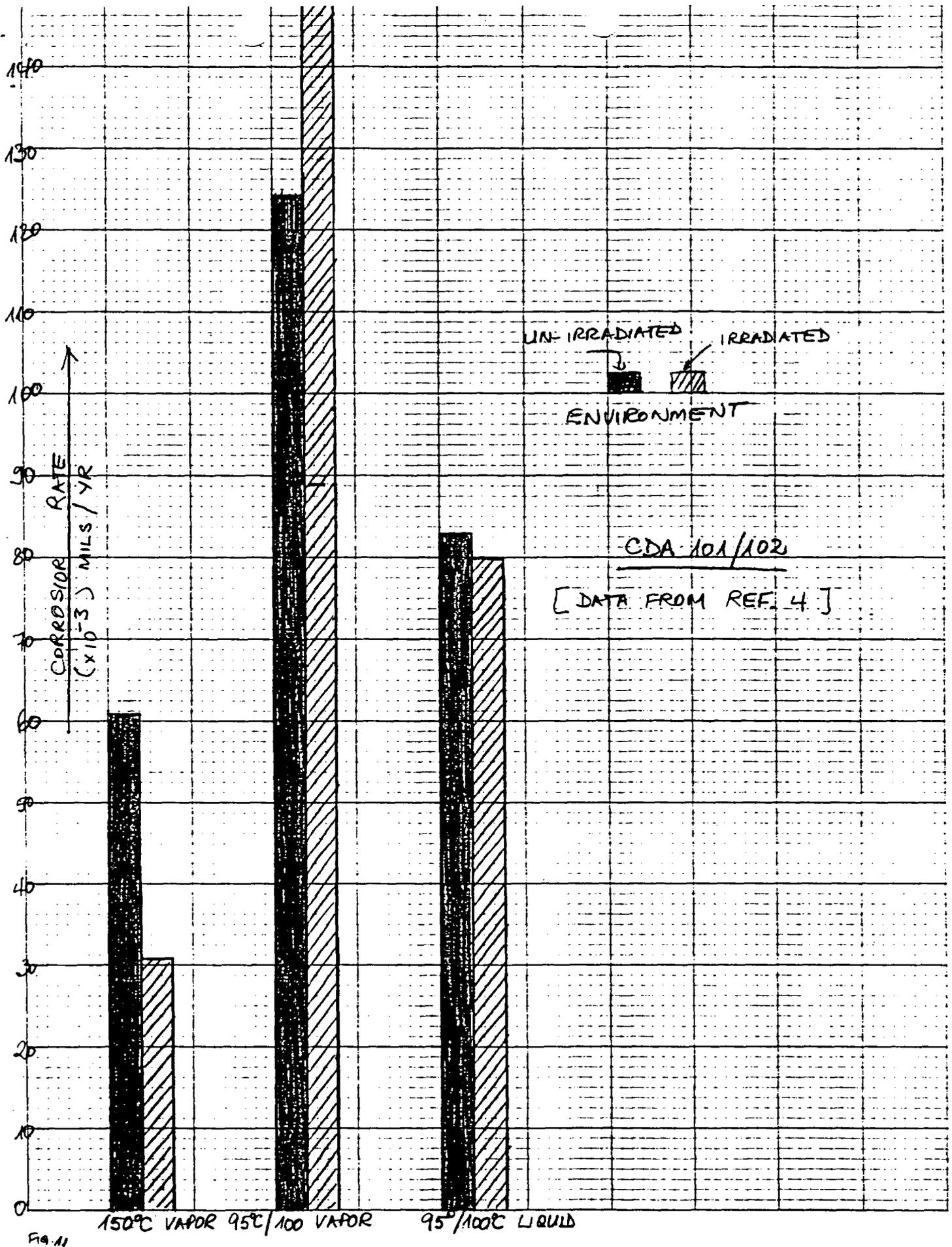


Fig. 11

Fig. 11. Comparison of Corrosion Rates of Alloy CDA101/102 in Irradiated and Un-irradiated Environments.

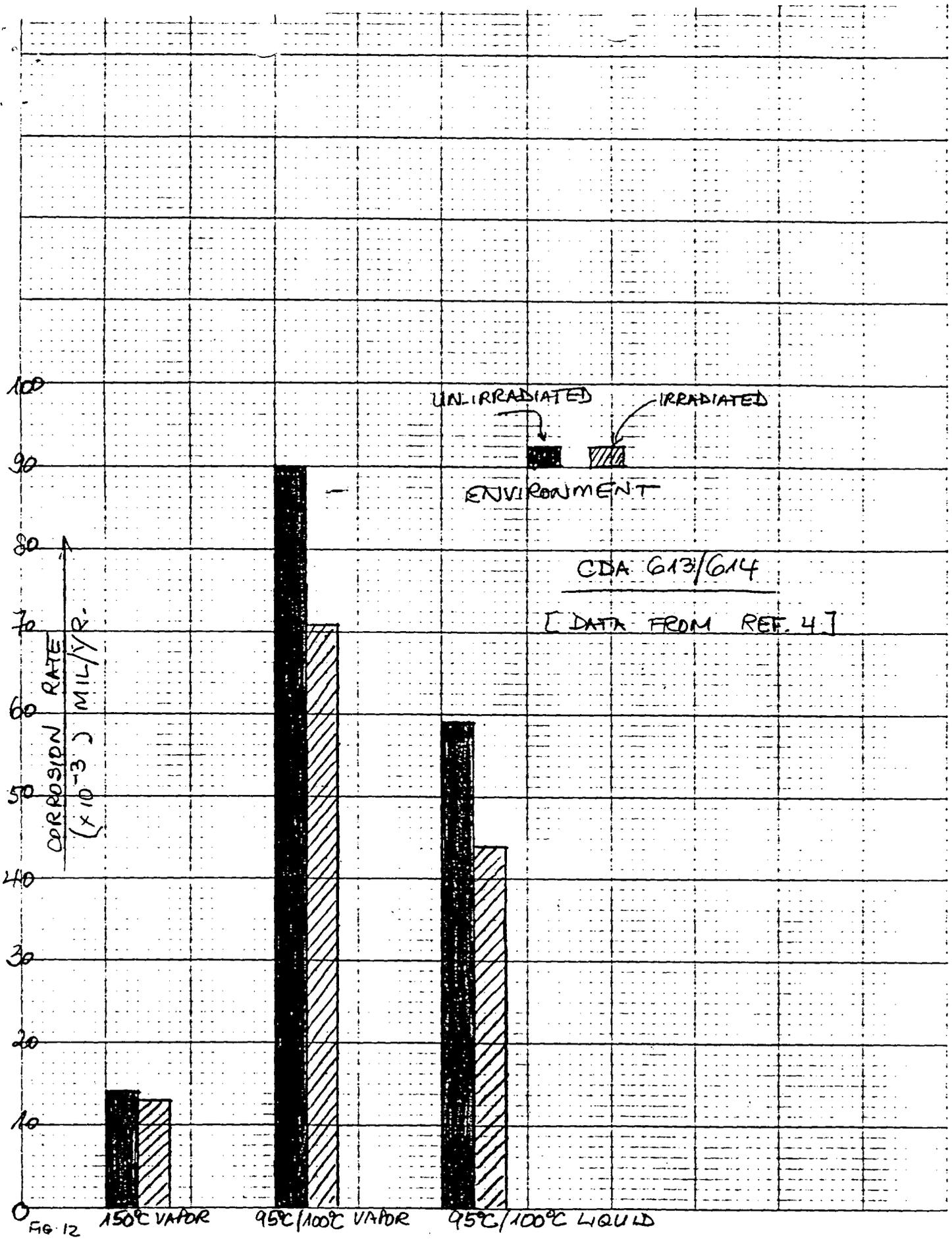


Fig. 12. Comparison of Corrosion Rates of Alloy CDA613/614 in Irradiated and Un-irradiated Environments.

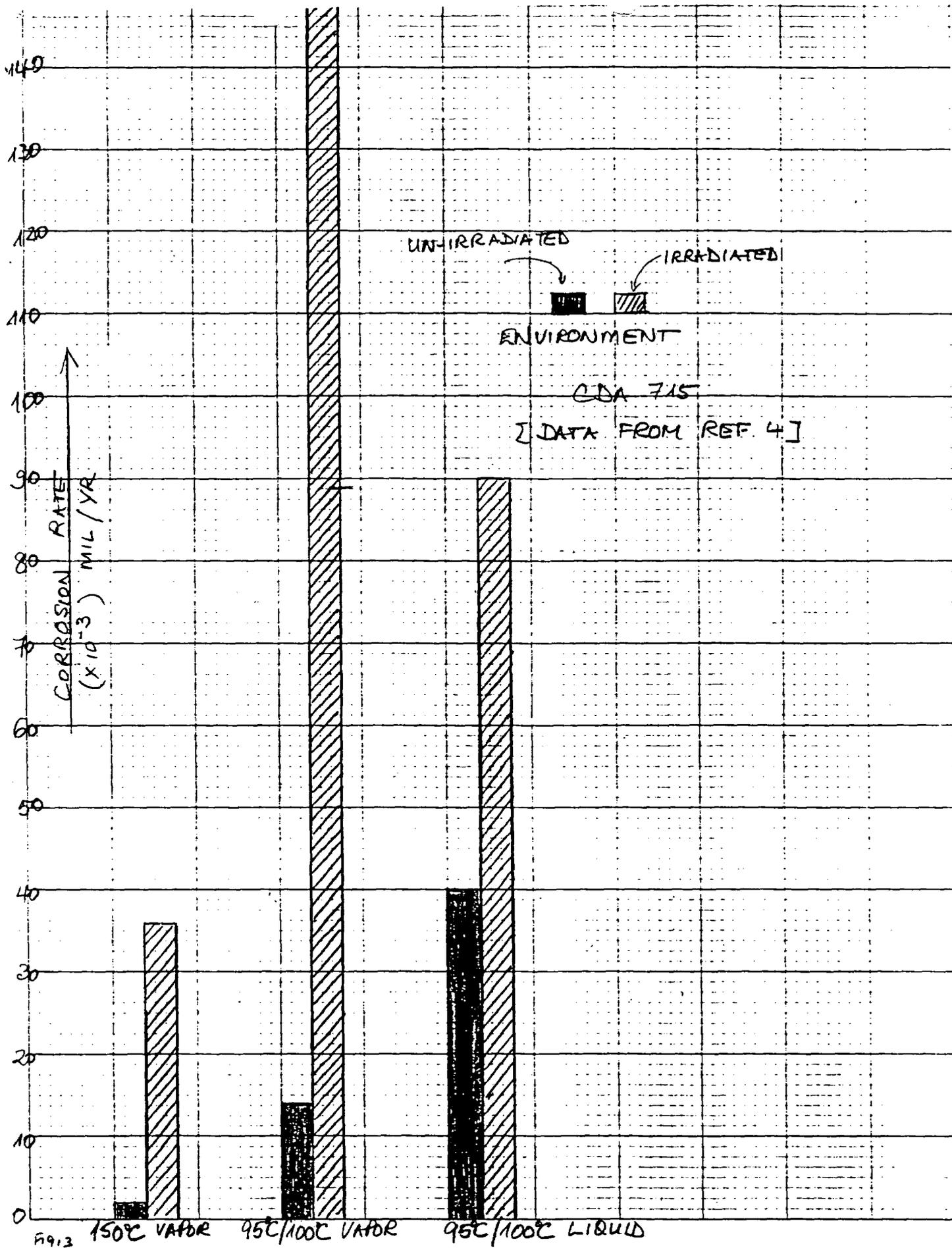


Fig. 13. Comparison of Corrosion Rates of Alloy CDA715 in Irradiated and Un-irradiated Environments.

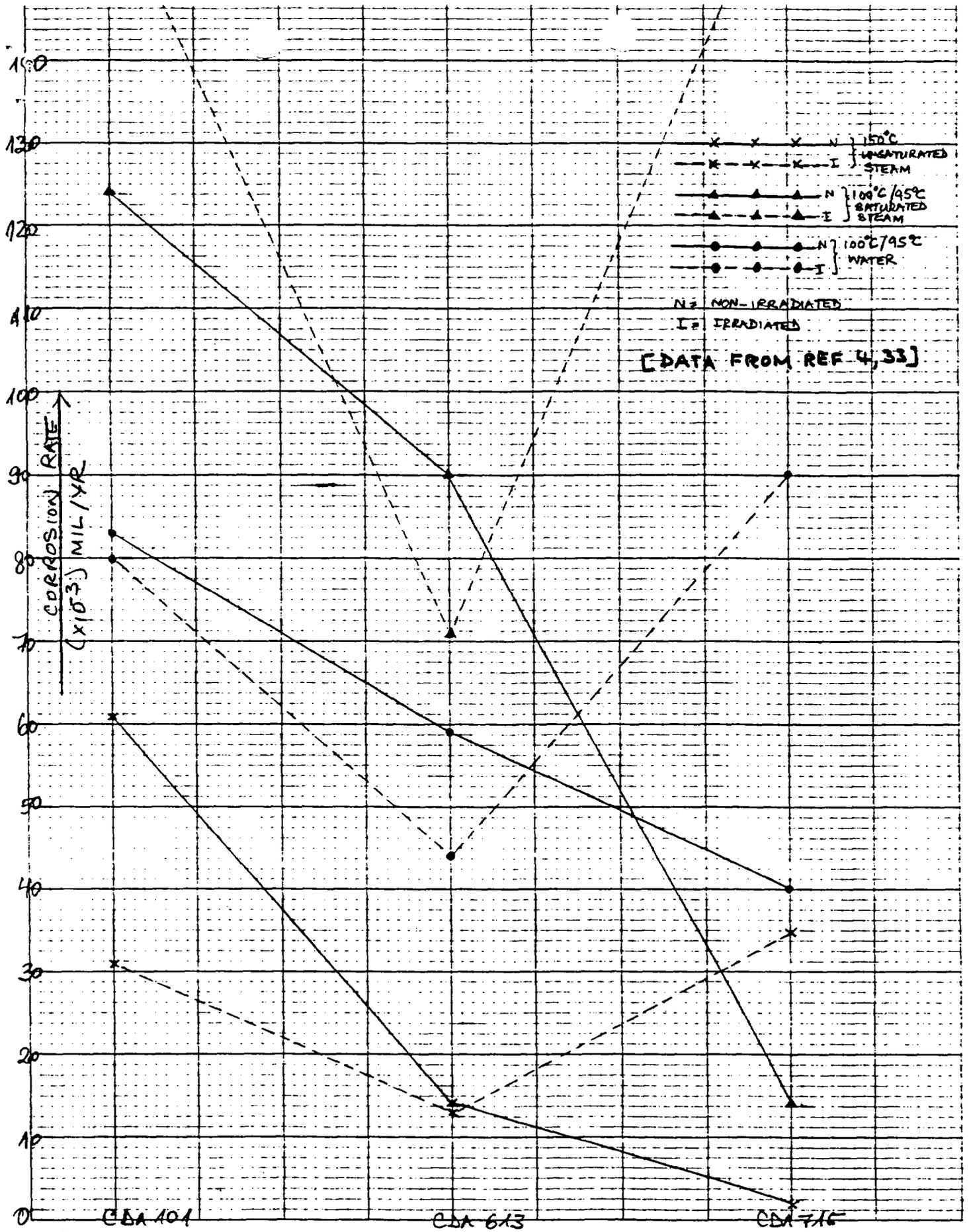


FIG 14

Fig. 14. Comparison of Corrosion Rates of Alloys CDA101/102, CDA613/614, and CDA715 as a Function of Irradiated and Un-irradiated Environments.