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CORROSION BEHAVIOUR OF SELECTED HIGH-LEVEL WASTE PACKAGING MATERIALS UNDER GAMMA IRRADIATION AND IN-SITU DISPOSAL CONDITIONS IN ROCK SALT

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Summary

Corrosion studies performed until now on a number of materials have shown that unalloyed steels, Hastelloy C4 and Ti 99.8-Pd are the most promising materials for a long-term resistant packaging to be used in high-level waste (HLW) canister disposal in rock salt formations. To characterize their corrosion behaviour in more detail, additional studies have been performed. The influence has been examined which is exerted by the gamma dose rate (1 Gy/h to 100 Gy/h) on the corrosion of three preselected steels and Hastelloy C4 at 90 °C in a salt brine (Q-brine) rich in $MgCl_2$, i.e., conditions relevant to accident scenarios in a repository. In addition, in-situ corrosion experiments have been carried out in the Asse salt mine at elevated temperatures (120 °C to 210 °C) in the absence and in the presence of a gamma radiation field of 3 x 10^2 Gy/h, within the framework of the German/US Brine Migration Test.

Under the test conditions the gamma radiation did not exert a significant influence on the corrosion of the steels investigated. No pitting and crevice corrosion or stress corrosion cracking occurred, and considering the corrosion rates of the steels (30 µm/a to 50 µm/a) the corrosion allowances for a thick walled packaging are acceptable. For these reasons the unalloyed steels continue to be considered as a promising packaging material. Hastelloy C4, exposed to dose rates of 10 Gy/h and 100 Gy/h, underwent pitting and crevice corrosion (20 µm/a at the maximum). Consequently, if this material were used, sufficient gamma shielding would have to be provided.

The low amounts of migrated salt brine (140 ml after 900 days) in the in-situ experiment did not produce noticeable corrosion of the materials.

Korrosionsverhalten von ausgewählten Verpackungsmaterialien für hochradioaktive Abfälle unter Gamma-Bestrahlung und in-situ-Endlagerbedingungen im Steinsalz

Zusammenfassung

Bisherige Korrosionsuntersuchungen an einer Reihe von Materialien ergaben, daß unlegierte Stähle, Hastelloy C4 und Ti 99,8-Pd die aussichtsreichsten Werkstoffe für eine korrosionsbeständige Verpackung zur Endlagerung von HAW-Kokillen in Steinsalzformationen sind. Zur weiteren Charakterisierung der Korrosion dieser Werkstoffe werden zusätzliche Untersuchungen durchgeführt. In dieser Arbeit wurde der Einfluß der Gammadosisleistung (1 Gy/h - 100 Gy/h) auf die Korrosion von drei vorausgewählten Stählen und Hastelloy C4 in einer bei Störfällen relevanten $MgCl_2$-reichen Salzlösung (Q-Lösung) bei 90 °C untersucht. Darüber hinaus wurden im Rahmen des Brine Migration Tests im Salzbergwerk Asse in situ-Korrosionsexperimente bei hoher Temperatur (120 °C - 210 °C) ohne und mit einem Gamma-Strahlenfeld von $3 \cdot 10^2$ Gy/h durchgeführt.

Unter den Prüfbedingungen hatte die Gammastrahlung keinen signifikanten Einfluß auf die Korrosion der untersuchten Stähle. Loch-, Spalt- oder Spannungsrißkorrosion traten nicht auf, und die Abtragsraten der Stähle (30 µm/a - 50 µm/a) führen zu akzeptablen Korrosionszuschlägen für eine dickwandige Verpakkung. Aus diesen Gründen werden die unlegierten Stähle weiterhin als ein aussichtsreicher Verpackungswerkstoff betrachtet. Bei Hastelloy C4 traten bei Dosisleistungen höher als 1 Gy/h Loch- und Spaltkorrosion (maximal 20 µm/a) auf. Daraus folgt, daß bei Verwendung dieses Materials eine ausreichende Gammaabschirmung erforderlich ist.

Die beim in situ-Experiment geringen Mengen an migrierter Lösung (140 ml nach 900 Tagen) führten zu keiner nennenswerten Korrosion der Materialien.

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1. Introduction

Radioactive waste disposal in deep rock salt formations is based on the concept of isolating radionuclides from the biosphere by combining geological with engineered barriers. For this multi-barrier concept the possibility is being studied at KfK of developing a long-term resistant packaging for HLW waste canisters to serve as a barrier during the high temperature phase (>100 °C) prevailing in the HLW disposal area for a few 10^2 years. The studies include qualification of a packaging material with long-term corrosion resistance in salt brines which may be present in rock salt as a result of thermal migration of brine inclusions or under accident scenarios in a repository.

The results of previous comprehensive corrosion studies /e.g. 1, 2, 3/ on a number of materials in salt brines have shown that unalloyed steels, Ti 99.8-Pd and Hastelloy C4 are the most promising materials for an HLW packaging. To characterise their corrosion behaviour in more detail, additional investigations are being performed. They focus on the unalloyed steels undergoing active corrosion because on these steels only general corrosion has been observed until now so that their long-term corrosion behaviour can be predicted more easily than that of the alloys Ti 99.8-Pd and Hastelloy C4 which undergo passive corrosion. Besides, the corrosion rates of the steels measured so far make corrosion allowances for a thick-walled packaging acceptable. Among the steels investigated until now - fine-grained steel, low-carbon steel and cast steel - fine-grained steel was selected as the reference steel because of its higher strength and better weldability and therefore priority will be given to studying this type of steel.

A major aspect in the corrosion studies is the determination of the influence of gamma radiation from the HLW on the corrosion of the packaging materials. In this work the corrosion behaviour of the three steels mentioned before and of Hastelloy C4 in a salt brine rich in $MgCl_2$ (Q-brine), which is relevant to accident scenarios, was studied for different dose rates (1 Gy/h - 100 Gy/h). Moreover, in the framework of the German/US Brine Migration Test in-situ corrosion experiments were performed in heated cased boreholes in the Asse salt mine under simulated HLW disposal conditions (high temperature, rock pressure and gamma radiation field). Besides steels, Hastelloy C4 and Ti 99.8-Pd, also nodular cast iron, Ni-Resist D4 and Si cast iron were investigated. The investigations of nodular cast iron, Ni-Resist D4 and Si-cast iron served to supplement the results previously obtained. A long-term barrier function cannot be expected from these materials because they have proved to be highly susceptible to local corrosion in previous laboratory-scale testing with brine excess /1/.

In addition to the packaging materials mentioned above, the Inconel 600 corrosion protection material to be used for the casing and the Al_2O_3 annular gap backfill material were examined for corrosion attacks under in-situ conditions.

2. Laboratory-scale corrosion studies under gamma irradiation

Investigations into the influence exerted by gamma radiation on the corrosion behaviour of HLW packaging materials are important for two reasons. First, radiolytic dissociation of salt brines produces reduced/oxidized reactive particles and stable products, e.g., e^-_{aq}, Cl_2^-, H_2O_2, O_2, ClO_4^-, ClO_3^-, Cl_2 /4, 5, 6/ which may accelerate the process of corrosion but may also inhibit it (formation of dense protective oxide layers /7/). Secondly, the semi-conductor properties of protective oxide

films of metals may be modified by absorption of the gamma radiation (radiation photo-effect) /6, 7/.

Preliminary studies /2, 3/ performed at 90 °C and a gamma dose rate of 1000 Gy/h (10^5 rad/h), based on the actual design of a thin-walled 5 mm thick HLW canister, have shown for unalloyed steels and Hastelloy C4 much higher general corrosion rates in salt brines than in the absence of irradiation. Moreover, heavy pitting and crevice corrosion up to 1 mm/a has been observed on Hastelloy C4. For a packaging serving as a barrier in the repository a wall thickness of about 100 mm is needed to make it stable against the rock pressure of about 40 MPa at 1000 m disposal depth. In this case, the expected dose rate on the surface of the packaging will be lower than 10 Gy/h. In the present work the corrosion behaviour of unalloyed steels and Hastelloy C4 has been studied at dose rates between 1 Gy/h and 100 Gy/h.

2.1 Materials investigated and types of specimen

The materials fine-grained steel (material no. 1.0566), low-carbon steel, cast steel (material no. 1.1131) and Hastelloy C4 (material no. 2.4610) were investigated. Their chemical compositions are given in Tab. 1. Fine-grained steel, low-carbon steel and Hastelloy C4 were delivered as hot rolled, annealed sheet metals, whereas cast steel was delivered as a cast slab. Compared with the fine-grained steel, the low-carbon steel has a lower content of C, Si and Mn; cast steel is the equivalent casting quality of fine-grained steel.

All materials were examined for general and pitting corrosion. In case of fine-grained steel and Hastelloy C4 the susceptibility to crevice corrosion and stress corrosion cracking and the influence of TIG (Tungsten Inert Gas) welding and electron beam

welding on their corrosion were studied in addition. Different types of specimen were used in the investigations.

To determine general corrosion non-welded plane specimens 40 mm x 20 mm x 4 mm and 40 mm x 10 mm x 10 mm (cast steel), respectively, in size were used. The influence of welding on corrosion was likewise determined on plane specimens with the welding seam running in the center normal to the longitudinal direction. The occurrence of stress corrosion cracking was studied on welded U-bend specimens (seam in the center of the specimen). The specimens used for crevice corrosion tests consisted of two plane specimens made of the relevant materials and brought into contact with a screw of the same material.

All specimens had been cleaned with alcohol in the ultrasonic bath before they were placed into the corrosion medium.

2.2 Testing conditions

The corrosion medium was a quinary salt brine (Q-brine) rich in $MgCl_2$. This solution must be expected in a hypothetical accident of inflow from remote disposal areas into the HLW boreholes of rather large amounts of brine included in rock salt. This type of solution is always present when potash seams are contacted. The corrosion medium had the following composition at 55 °C (in wt.%):

26.8% $MgCl_2$, 4.8% KCl, 1.4% $MgSO_4$, 1.4% NaCl, 65.7% H_2O.

To simulate redissolution of pure NaCl at the higher repository temperatures prevailing in an HLW borehole ($\leqslant$200 °C) 1.7 g NaCl were added per 100 g solution. The measured pH-value and O_2 saturation value of the solution were 4.1 and 3.7 mg/l, respectively, at 25 °C.

Low-carbon steel and cast steel were examined at gamma dose rates of 1 Gy/h and 10 Gy/h, which are realistic values for the containers discussed here of at least 100 mm wall thickness. The fine-grained reference steel and Hastelloy C4 were subjected to a more stringent additional test at 100 Gy/h. The radiation source were spent fuel elements of different degrees of burnup (cf. section 2.3).

The test temperature was selected to be 90 °C in order to have a direct comparison with the results of the previous investigations performed at this temperature and 1000 Gy/h /2, 3/. At this temperature it was possible to carry out the experiments at normal pressure because it is sufficiently well below the boiling point of the solution (about 115 °C). Experiments conducted at the maximum HLW disposal temperature ($\lesssim$ 200 °C) are under way. The experiments were made at a ratio of specimen surface to brine volume (S/V ratio) of 20 m^{-1} which means that the corrosion medium was present in excess. The test duration was varied between 50 days and 12 months.

2.3 Experimental set-up

The corrosion experiments were performed with various gamma dose rates in the spent fuel element storage pool of KFA Jülich. The radiation source were spent fuel elements of different degrees of burnup. The experimental set-up has been represented schematically in Fig. 1. The material specimens and the corrosion medium (salt brine) were contained in tubular vessels made of Duran glass and directly connected with cooling coils in order to allow the steam to condense. The cooling coils end in the vapour space of a water-filled cylindrical container whose partial pressure corresponds to the water temperature of 24 °C. The specimen accommodating vessels are suspended in a circular configuration in water-tight cylindrical stainless steel containers (irradiation containers) placed in a rack likewise made

of stainless steel. Each of the four containers can accommodate up to 30 specimen vessels with 3 specimens each. Figures 2 and 3 show the irradiation containers and their components. The bottom part of the container is made double-walled and insulated with glass wool. The top part of the container accommodates the cooling coils and the connections for current and cleansing gas supply as well as the measuring instruments. The cleansing gas (He) served to discharge into the atmosphere the radiolytic gases and gaseous corrosion products generated during the experiment.

For irradiation the containers were positioned on the bottom of the 6 m deep water-filled spent fuel-element storage pool. The fuel elements serving as radiation source were arranged symmetrically around the respective container in order to achieve a homogeneous radiation field. The dose rate in the specimen area during the experiment was monitored by a high performance dosimeter. The specimens were heated to the 90 °C test temperature with cartridge type heaters, the temperatures were measured with thermocouples.

2.4 Methods used in post-test examinations

After removal from the corrosion medium the specimens were freed from the adhering salts and corrosion products by pickling in suitable solutions according to ASTM guidelines /8/. Then the specimens were cleaned in alcohol and examined for general and local corrosions as well as for stress corrosion cracking. The general corrosion (integral corrosion rate) was calculated from the integral weight losses determined by gravimetry and from the respective material densities. The specimens were examined for local corrosion and stress corrosion cracking by microscopic evaluation and with the help of metallographic cross-sections, measurements of pit depths and surface profiles.

2.5 Results and discussion

The dependence on time of the general corrosion rates of the steels in Q-brine at different dose rates has been plotted in Fig. 4. For comparison, also the values determined in earlier studies /2/ without irradiation and at 1000 Gy/h, respectively, have been entered. The corrosion rates are mean values of three to six specimens and they have been calculated from the weight losses determined by gravimetry. The ranges of the corrosion rates represented as bars show the standard deviations of the measured values.

At a dose rate of 1000 Gy/h, which is to be expected to occur on the surface of a thin-walled HLW canister (about 5 mm wall thickness), the corrosion rates of fine-grained steel (460 µm/a) and cast steel (660 µm/a) are higher by approximately the factor 15 than the values obtained without irradiation. At lower dose rates between 1 Gy/h and 100 Gy/h, which are relevant to the thick-walled packaging discussed here, the corrosion rates of the fine-grained steel are only about 20 µm/a - 40 µm/a and thus close to the value without irradiation (30 µm/a). In the case of cast steel and low-carbon steel the corrosion rates at 1 Gy/h and 10 Gy/h of about 20 µm/a - 30 µm/a are lower than those without irradiation (40 µm/a - 80 µm/a). The reason for this effect is not yet known.

The metallographic examinations have shown that the steels underwent non-uniform corrosion between 1 Gy/h and 100 Gy/h which is attributed to the inhomogeneity of their composition. The maximum penetration rates measured have been given in Tab. 2. For comparison, also the values determined in our earlier studies without irradiation and at 1000 Gy/h, respectively, have been entered. At a dose rate of 1000 Gy/h the penetration rates of 500 µm/a to 700 µm/a are significantly higher than the values without irradiation (40 µm/a - 50 µm/a), as already reported /2, 3/. In the range between 1 Gy/h and

100 Gy/h the penetration rates are only 30 µm/a to 50 µm/a and by approximately the factor 1.5 higher than the average corrosion rates. Penetration rates of this size imply acceptable corrosion allowances for a thick-walled packaging. Moreover, the steels were resistant to pitting and crevice corrosion and to stress corrosion cracking in Q-brine at 90 °C. Welding did not exert a noticeable influence on their corrosion behaviour. Figures 5 and 6 show optical micrographs of fine-grained steel and cast steel with non-uniform corrosion in Q-brine at 1000 Gy/h and 10 Gy/h, respectively.

The results of investigations into general and local corrosion of Hastelloy C4 in Q-brine at 90 °C and with dose rates of 1 Gy/h - 100 Gy/h have been compiled in Tab. 3. For comparison, also the results of the previous investigations carried out both without irradiation and with 1000 Gy/h have been entered. At dose rates between 1 Gy/h and 100 Gy/h the maximum corrosion rates of 0.4 µm/a are low and roughly correspond to the value obtained in the absence of irradiation. The dose rate in this range did not noticeably influence the corrosion rate. Moreover, this material remained resistant to stress corrosion cracking and local corrosion even after 12 months exposure to 1 Gy/h. Also when exposed to 10 Gy/h and 100 Gy/h, Hastelloy C4 proved to be resistant to stress corrosion cracking; but at these dose rates pitting and crevice corrosion of 20 µm/a at the maximum was detected. The penetration rate remained unchanged during the whole testing period of 12 months. At the dose rate of 1000 Gy/h strong pitting and crevice corrosion occurred as already indicated in previous publications /2/, the maximum penetration rate being about 1 mm/a. Figures 7 and 8 show characteristic optical micrographs of Hastelloy C4 after 12 months immersion in Q-brine (90 °C) and exposure to 1 Gy/h (uniform corrosion) and 10 Gy/h (pitting corrosion of about 20 µm/a).

3. In-situ corrosion studies

In addition to laboratory-scale corrosion studies carried out under hypothetical accident conditions, in-situ corrosion experiments are being performed under normal operating conditions in the Asse salt mine on specimens and welded tube sections made of selected materials. The materials investigated are: unalloyed steels, Ti 99.8-Pd, Hastelloy C4 and iron base alloys such as nodular cast iron, Si-cast iron and Ni-Resist D4. The following investigations are being performed:

a) Investigations of material specimens stored in the loose rock salt at rock temperature (reference experiments)

- maximum temperature: 32 °C,
- type of specimen: plane, non-welded and welded,
- testing period: 1-5 years, beginning April 1983.

b) Investigations of material specimens stored in 6 m deep boreholes at the HLW elevated temperature with and without gamma radiation field (performed in the framework of the Brine Migration Test)

- maximum temperature: 210 °C,
- gamma dose rate: 3×10^2 Gy/h (γ-E: 1.1+1.3 MeV, Co-60),
- rock pressure: 28 MPa at the maximum,
- brine migration, gas constituents from the rock salt,
- type of specimen: plane, non-welded and welded,
- testing period: about 3 years, beginning December 1983.

c) Investigations of tube sections stored in 2 m deep boreholes at the HLW design temperature

- maximum temperature: 200 °C,
- rock pressure: <20 MPa,
- brine migration, gas constituents from the rock salt,

- type of specimen: electron beam welded tube sections for simulating a container closure technique (diameter = 40 mm, length = 500 mm, thickness = 10 mm),
- testing period: 1-3 years, beginning March 1985.

d) Investigations of material specimens in 15 m deep boreholes at elevated temperature and in a gamma radiation field (HLW test disposal)

- maximum temperature: 250 °C,
- maximum gamma dose rate: 5×10^2 Gy/h (γ-E: about 0.7 MeV, Cs/Ba-137),
- maximum rock pressure: 50 MPa,
- brine migration, gas constituents from the rock salt,
- type of specimen: plane, non-welded and welded,
- testing period: 5 years, beginning 1988.

The corrosion investigations b) and d) are the KfK contributions to the borehole experiments /9, 10/ carried out by the Institut für Tieflagerung of Gesellschaft für Strahlen- und Umweltforschung (GSF, Munich). Detailed information about these in-situ corrosion experiments is given in /11/.

This paper is a report on the investigations carried out in the framework of the Brine Migration Test (item b) at the HLW design temperature and at rock pressure, with and without gamma radiation field.

3.1 Materials investigated and types of specimen

The chemical compositions of the materials investigated - Ti 99.8-Pd, Hastelloy C4, fine-grained steel, cast steel, nodular cast iron, Si-cast iron and Ni-Resist D4 - are shown in Tab. 4. The materials Ti 99.8-Pd and Hastelloy C4 were investi-

gated as delivered (hot-rolled sheet metals, annealed, descaled) without any subsequent surface treatment. Ti 99.8-Pd, as a result of the manufacturing process, exhibited an approx. 200 - 400 µm thick deformation layer which was covered by a uniform oxide layer (50 - 100 nm thickness). Before corrosion testing the specimens made of fine-grained steel (hot-rolled and annealed sheet metal), cast steel and nodular cast iron were freed from the adhering oxide layer and cast skin, respectively, by milling. The material specimens made of Ni-Resist D4 and Si cast iron were investigated in the as-delivered condition, i.e., with a surface ground allround.

All materials were examined for their resistance to general corrosion (weight change) and local corrosion. Plane specimens with the following dimensions were used: Ti 99.8-Pd, Hastelloy C4 and fine-grained steel 40 mm x 20 mm x 3-4 mm; Si cast iron 36 mm x 18 mm x 5 mm; and the rest of cast materials 40 mm x 10 mm x 10 mm.

The materials cast steel, nodular cast iron, Ni-Resist D4 and Si cast iron were investigated exclusively in the as-delivered condition. For the most promising HLW packaging materials fine-grained steel, Ti 99.8-Pd and Hastelloy C4 the influence of welding on their corrosion behaviour was also studied with a view to container welding in later application. For this purpose, specimens were examined with a TIG (Tungesten Inert Gas) weld bead applied. In order to test the suitability of Hastelloy C4 as a container material for direct filling of HLW glass, some of the specimens were subjected to thermal treatment either before or after welding. This simulated the loading of the bottom and lid welds in practical application. The thermal treatment of the specimens was described in an earlier publication /1/.

All material specimens were cleaned in alcohol in an ultrasonic bath before they were stored. After storage the specimens were freed from the adhering salts and corrosion products using suitable pickling solutions and then their corrosion attack was investigated.

The weight change of the specimens after corrosion was determined by gravimetry. The depth of any local corrosion attacks was determined with an electronic depth gauge as well as from surface profiles and metallographic transverse sections.

3.2 Testing conditions

The material specimens to be investigated were stored in four heated, cased boreholes (test sites 1-4). In two of them (test sites 3 and 4) Co-60 sources had been installed. The casing material was a refractory steel with Inconel 600 clad as a corrosion protection.

The approximately 5 cm wide annular space between the casing and the borehole wall was filled with Al_2O_3 spheres in the bottom part of the borehole in order to prevent the salt from contacting the casing and, on the other hand, maintain the porosity of the annular space for measurement purposes. In the test sites 2 and 4 a gas flow (N_2) was permanently passed through the annular space and in the test sites 1 and 3 only at the end of the test. This gas flow carried to the cooling trap the water released by migration into the borehole. With these conditions selected for the tests the initial phase of disposal was simulated, i.e., the period of about 2 years /12/ until closure of the annular gap between the HLW package and the borehole wall.

A detailed description of the test set-up is given in /13/. The longitudinal section of one of the storage boreholes as well as the corrosion conditions to which the specimens were exposed have been represented in Fig. 9.

It can be noticed that under the selected conditions the brine migrating into the boreholes evaporated so that the specimens were exposed to a steam atmosphere with salt constituents. Besides, gases emanating from the rock salt participated in the corrosion process in addition to gaseous products generated during corrosion of the materials and radiolysis of the brine. The measured values of the volume and composition of the brine and gas, represented in Fig. 9, as well as the temperature profile and the pressure building up are maximum and minimum values applicable to all four boreholes. They were determined by the Institut für Tieflagerung, Braunschweig. Detailed information about the development versus time of the measured values is given in /13/ which includes also information about the distribution of the specimens in the boreholes. The materials were tested at temperatures between 120 °C and 210 °C. The testing temperatures for the individual materials are given in Tab. 5. The maximum gamma dose rate was 3×10^2 Gy/h and the calculated maximum rock pressure was 28 MPa. The maximum testing period for the materials was about 900 days.

3.3 Results and discussion

The materials tested corroded at extremely low rates under the in-situ testing conditions, both in the presence and in the absence of gamma radiation. No noticeable influence has been observed of TIG welding or thermal treatment of Hastelloy C4 on the corrosion behaviour of the materials. The weight losses of the materials determined by gravimetry and the linear corrosion rates calculated from them have been entered in Tab. 5. Some specimens did not lend themselves to gravimetric evaluation

because they had been damaged mechanically in the course of retrieval. These specimens were used for local corrosion examinations. It is apparent from Tab. 5 that the corrosion rates of all materials not exposed to irradiation, are <2 µm/a and that, except for fine-grained steel, gamma radiation of $3x10^2$ Gy/h has not resulted in an increase of these values.

The low corrosion rates of the materials can be explained by the fact that only 140 ml brine at the maximum had flown into the boreholes by migration which spread over the large surface of the inserts (casing, etc.) of about 71 m^2. Therefore, only a very low amount of brine was available for the material specimens of a maximum surface of 250 cm^2 to corrode.

The higher corrosion rate determined for fine-grained steel exposed to irradiation (about 14 µm/a) is probably not caused by the effect of radiation. This assumption relies on the finding that for the similar material, cast steel, there was no difference in the corrosion rates with and without gamma radiation. The increase in the corrosion rate is probably attributable to the fact that after the heater had been shut down because of plugging of a tube it was not possible to condense more than about half of approx. 1600 ml of inflowing brine. Thus, these specimens suffered corrosion attack by non-condensed brine for an additional period of approx. 12 months (i.e., the time interval between shut-down of the heater and specimen retrieval) at a mean temperature of about 70 °C.

The metallographic examination of the specimens has shown that, with the exception of fine-grained steel exposed to irradiation, all the other materials undergo uniform corrosion under the in-situ conditions. Figures 10 and 11 show by way of example micrographs of Ti 99.8-Pd, Hastelloy C4 and fine-grained steel before and after storage. In case of fine-grained steel a

non-uniform corrosion attack with a maximum penetration rate of about 25 µm/a was observed which is attributed to corrosion through non-condensed brine as already discussed.

The comparison of the results from in-situ corrosion experiments with those from laboratory-scale studies shows:

- The corrosion rates of the iron base alloys investigated in-situ have been much lower than those obtained in laboratory-scale experiments /14/ with brine in excess.

- For Ti 99.8-d and Hastelloy C4 only negligible differences have been found between laboratory and in-situ results of corrosion rates.

- The very pronounced local corrosion attacks on nodular cast iron, Ni-Resist D4, Si-cast iron and Hastelloy C4 (only at 200 °C and under irradiation at 1000 Gy/h), respectively, observed in the laboratory-scale experiments have not occurred under the in-situ conditions.

Metallographic and scanning electron microscope examinations of selected material specimens taken from the four casings have not indicated any measurable corrosion attack. Furthermore, semi-quantitative examinations using EDAX (Energy Dispersive X-Ray Analysis) have not made evident a change in the Fe, Cr and Ni contents compared with the initial material.

H_2S, which is present in low amounts in rock salt /15/, was not detected in the gas analyses conducted in the boreholes 1 to 4. Two indications of the supposed reaction taking place between nickel from Inconel 600 and hydrogen sulphide to give NiS have been found with the help of EDAX:

- Contrary to the starting material, sulphur has been detected in the transverse sections of the Inconel specimens.

- Sulphur has likewise been identified to be present on the surface of an Inconel specimen taken from borehole 4.

The H_2 concentrations of 2.2 vol.% measured in the boreholes cannot be explained by the very low corrosion of the material specimens. Hydrogen is probably generated during corrosion of the Inconel 600 casting material, since for a surface of about 3 m^2 minor general corrosion of a few tenths of a micrometer would already lead to significant amounts of H_2. Such small reductions of material thickness could not be detected by the methods used here. They require more sophisticated methods.

These methods are:

- Auger Electron Spectroscopy (AES),
- Electron Spectroscopy for Chemical Analysis (ESCA),
- X-ray Photoelectron Spectroscopy (XPS).

Micrographs of Al_2P_3 spheres from all boreholes have not exhibited noticeable modifications compared with the initial state. No attack of the grain boundaries of Al_2O_3 spheres by penetrating constituents of the migrating brine (e.g., Na, Cl) similar to that found in the laboratory-scale experiments /16/ conducted on the Al_2O_3 material in Q-brine has been detected in the examinations relying on EDAX.

4. Conclusions

- At gamma dose rates between 1 Gy/h and 100 Gy/h no significant influence has to be expected from radiation on the corrosion of the unalloyed steels investigated which were kept in Q-brine at 90 °C. It should be mentioned that in earlier

investigations carried out at the very high dose rate of 1000 Gy/h an increase in corrosion rates by approximately the factor 15, compared with the values without irradiation, had been found.

- Under the conditions above comparable corrosion rates (30 µm/a - 50 µm/a) for the steels and acceptable corrosion allowances for the thick-walled HLW packaging discussed have to be anticipated. Pitting and crevice corrosion in the sense of an active-passive corrosion element or stress corrosion cracking have not to be expected on the basis of results available.

- For Hastelloy C4 it has been shown in agreement with previous electrochemical /17/ and irradiation /2/ experiments that the material, in the presence of strong oxidants (e.g., H_2O_2, ClO_3^-) from radiolysis of the Q-brine, is sensitive to local corrosion. Already at 10 Gy/h and 90 °C attacks by pitting and crevice corrosion occurred. This means that if Hastelloy C4 is used as an HLW packaging material an adeqaute gamma shield will be required.

- The in-situ investigations have shown that during the initial phase of disposal, i.e., as long as a gap exists between the HLW packaging and the borehole wall, no noticeable corrosion has to be expected of the packaging materials from limited volumes of migrating brine. This is true above all for Ti-99.8-Pd and Hastelloy which undergo passive corrosion and in which local corrosion could be caused already by minor volumes of brine.

The results available on corrosion in Q-brine at 90 °C and at gamma dose rates between 1 Gy/h and 10 Gy/h have confirmed that unalloyed steels are a promising material. For this reason, the detailed studies on the fine-grained steel, the reference steel, will be continued. These studies will focus above all on

clarifying the role which elevated temperature ($\leqslant$ 200 °C) plays during corrosion under gamma irradiation. Moreover, the in-situ corrosion experiments on tube sections with simulated container closure (electron beam welding) will be carried on at the elevated temperature of 200 °C.

5. References

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Table 1 Chemical Compositions of Materials Used in Laboratory Scale Corrosion Experiments

Material	Composition (wt.-%)									
	C	Si	Mn	P	S	Cr	Ni	Mo	Ti	Fe
Fine-grained steel Material No. 1.0566	0.17	0.44	1.49	0.021	0.004	-	-	-	-	Bal.
Low-carbon steel	0.1	0.27	0.66	0.018	0.001	-	-	-	-	Bal.
Cast steel Material No. 1.1131	0.16	0.61	1.51	0.024	0.014	-	-	-	-	Bal.
Hastelloy C4 Material No. 2.4610	0.006	0.05	0.09	-	-	15.4	Bal.	15.2	0.24	0.79

- = not existing or negligible

Table 2 Maximum Penetration Rates of Non-Uniform Corrosion of Unalloyed Steels after 1 Year Immersion in Q-Brine at 90°C with and without Gamma-Irradiation

Material	Maximum Penetration Rate [µm/a]				
	without Gamma	1 Gy/h	10 Gy/h	100 Gy/h	1000 Gy/h
Fine-grained steel	40	30	40	40	500
Low-carbon steel	90	40	50	-	-
Cast steel	50	30	30	-	700

- = not investigated

Table 3 Average General Corrosion Rates and Maximum Pitting Rates of Hastelloy C4 after 1 Year Immersion in Q-Brine at 90°C with and without Gamma-Irradiation

Dose Rate (Gy/h)	Average General Corrosion Rate [µm/a]	Maximum Pitting Rate [µm/a]
0	0.1	-
1	0.05	-
10	0.4	20
100	0.4	20
1000	3.5	1000

- = uniform corrosion

Table 4 Chemical Composition of the Materials Used in the In-situ Corrosion Experiments

Material	Composition (wt.-%)												
	Cr	Ni	Mo	Ti	Pd	C	Si	Mn	Nb	O_2	N_2	H_2	Fe
Ti 99.8 Pd Material No. 3.7025.10	-	-	-	Bal.	0.17	0.01	-	-	-	0.04	0.01	0.001	0.05
Hastelloy C4 Material No. 2.4610	16.8	Bal.	15.9	0.33	-	0.006	0.05	0.09	-	-	-	-	0.05
Fine-grained steel Material No. 1.0566	-	-	-	-	-	0.17	0.44	1.49	-	-	-	-	Bal.
Cast steel Material No. 1.1131	-	-	-	-	-	0.16	0.61	1.51	-	-	-	-	Bal.
Nodular cast iron Material No. 0.7043	-	-	-	-	-	3.7	1.83	0.21	-	-	-	-	Bal.
Ni-Resist D 4 Material No. 0.7680	5.5	30.9	-	-	-	2.6	4.25	0.5	-	-	-	-	Bal.
Si-Cast iron	-	-	-	-	-	0.72	15.0	0.62	-	-	-	-	Bal.

- = not existing or negligible

Table 5 Weight Loss and Corrosion Rate of the Materials Used in the In-situ Corrosion Experiments with and without Gamma-Irradiation

Material	Test Temperature (^{o}C)	Without Gamma-Irradiation (Exposure Time: 900 d)		With Gamma-Irradiation $3 \cdot 10^2$ Gy/h (Exposure Time: 700 d)	
		Weight Loss (g/m^2)	Corrosion Rate ($\mu m/a$)	Weight Loss (g/m^2)	Corrosion Rate ($\mu m/a$)
Ti 99.8 Pd	210	+	+	1.4	0.16
Hastelloy C4	210	+	+	19.19	1.18
Fine-grained steel	150	17.79	0.95	200.06	13.68
Cast steel	150	22.72	1.18	9.49	0.63
Ni-Resist D4	150	5.43	0.29	3.23	0.22
Nodular cast iron	120	+	+	13.26	1.01
Si-cast iron	120	29.31	1.72	+	+

+ = Specimens not retrievable or mechanically damaged

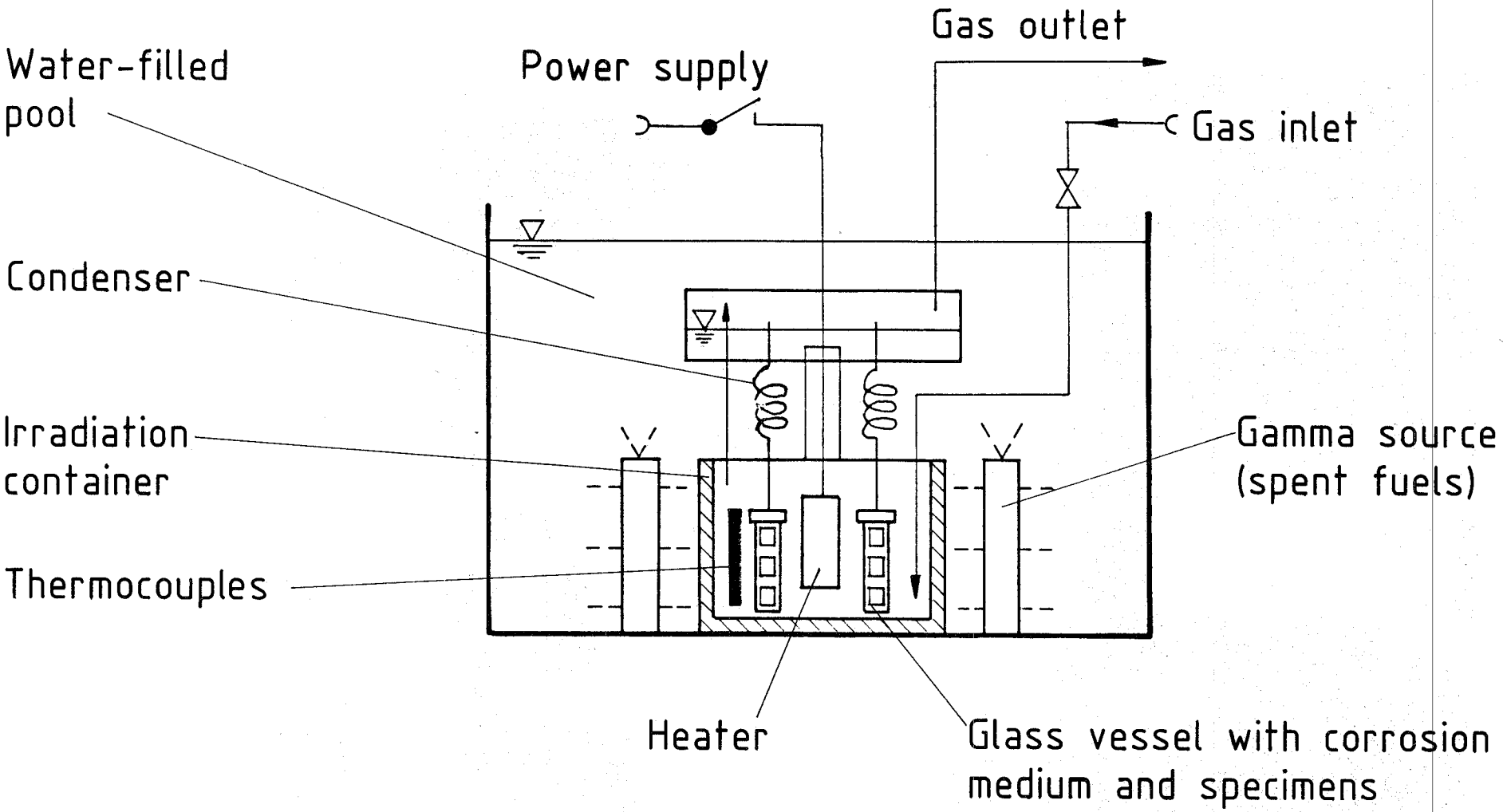


Fig. 1 : Schematic of test facility for corrosion experiments under gamma irradiation at 90°C.

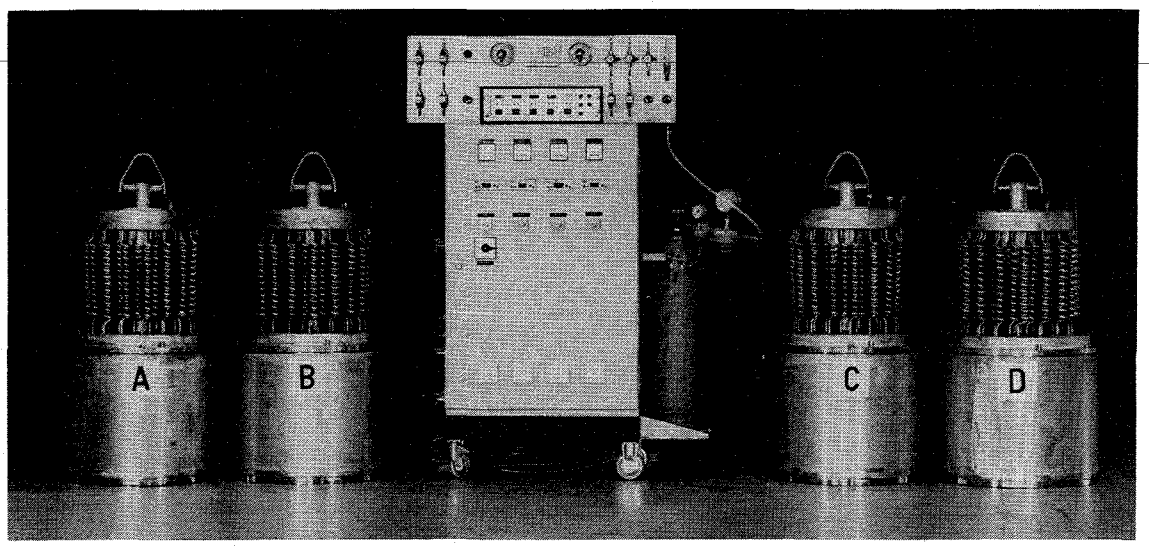


Fig. 2 Irradiation vessel; electricity and cleansing gas supply

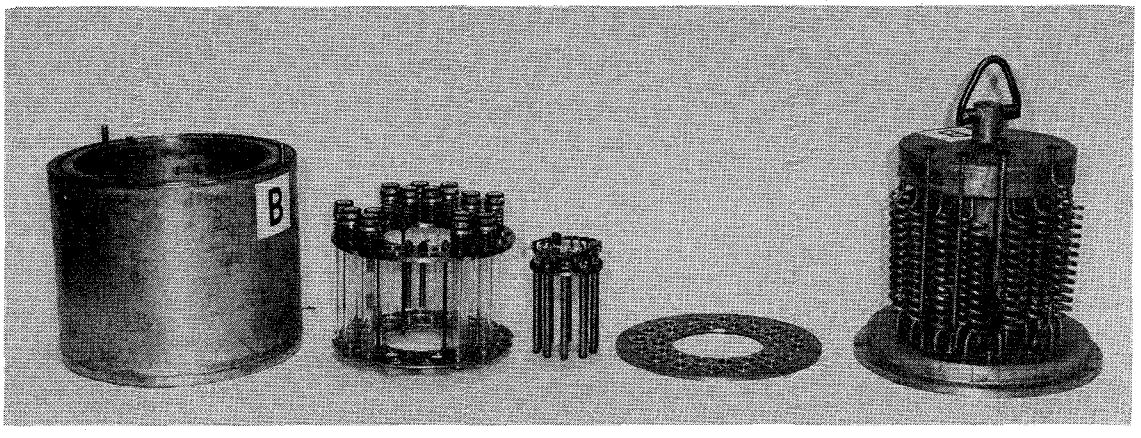


Fig. 3 Components of an irradiation vessel (from left to right: vessel bottom part, specimen rack, heating system, sealing disk and vessel top part with cooling coils)

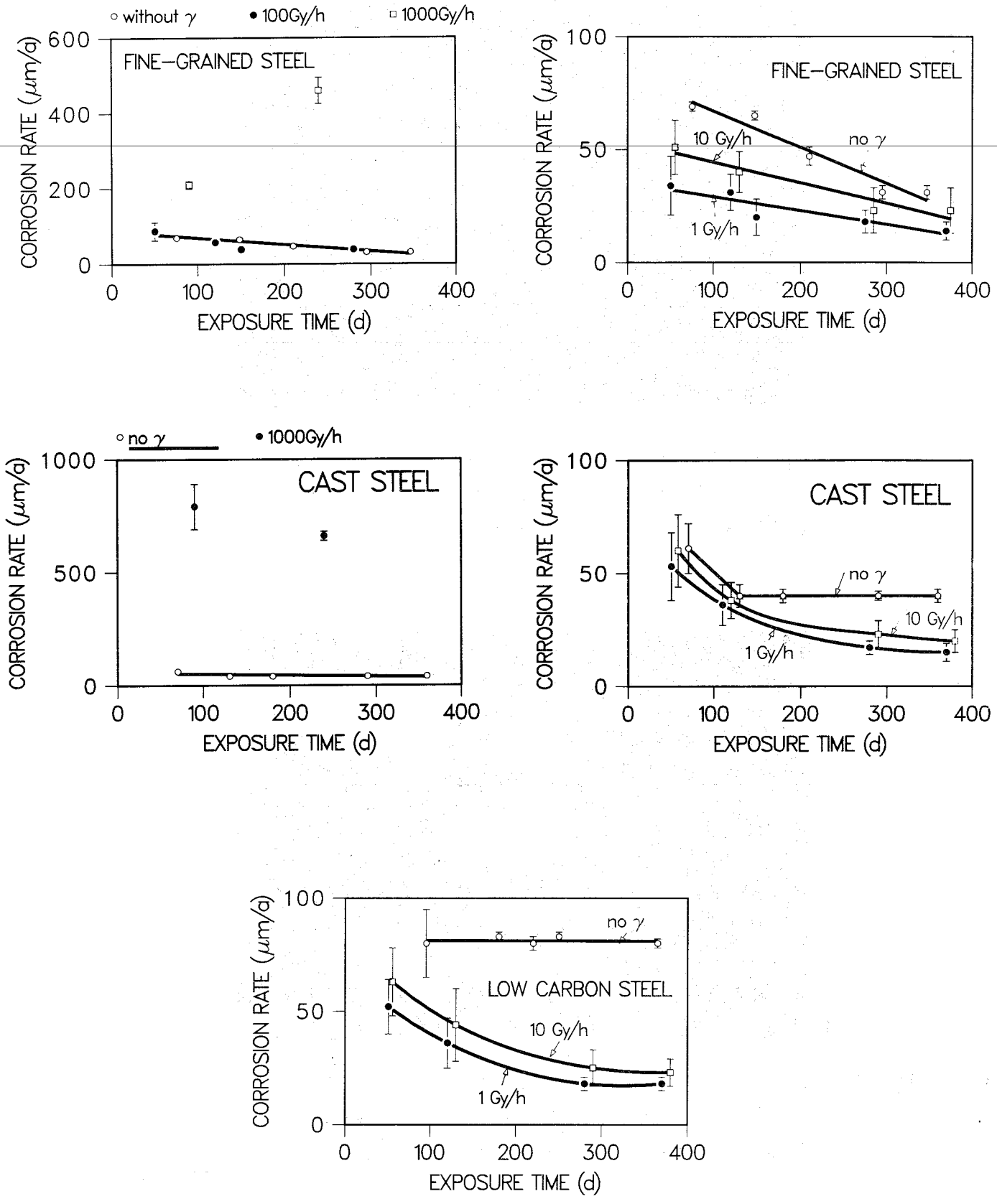
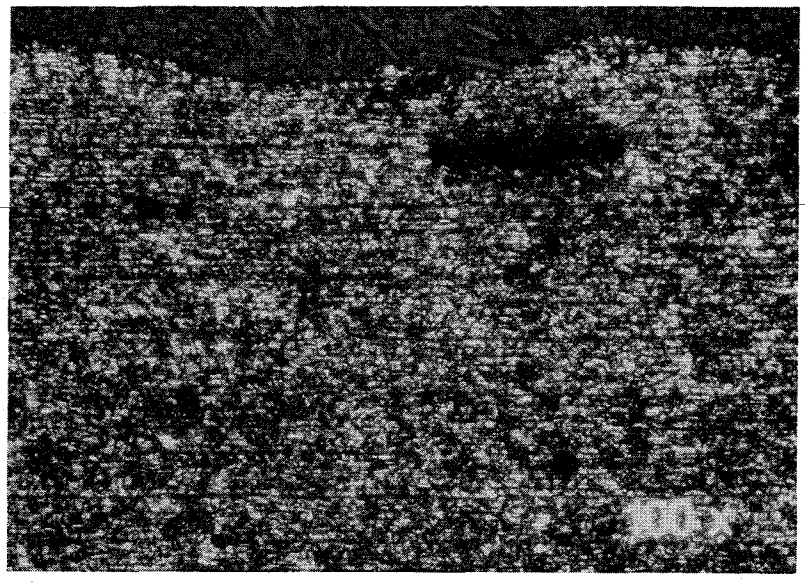


Fig. 4: Average general corrosion rates of unalloyed steels in Q-brine at 90°C with and without gamma irradiation

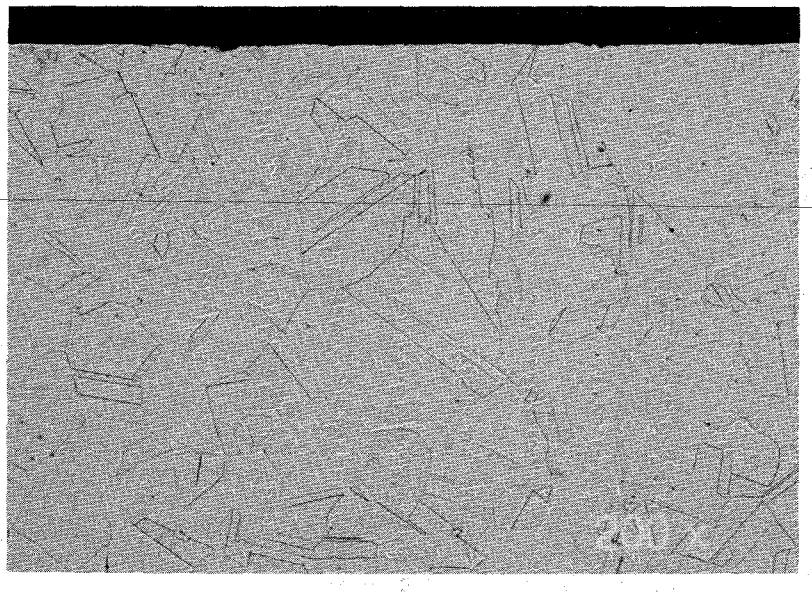


X 100

Fig. 5 Optical micrograph of fine-grained-steel after 275 days immersion in Q-brine at 90°C and a gamma dose rate of 100 Gy/h

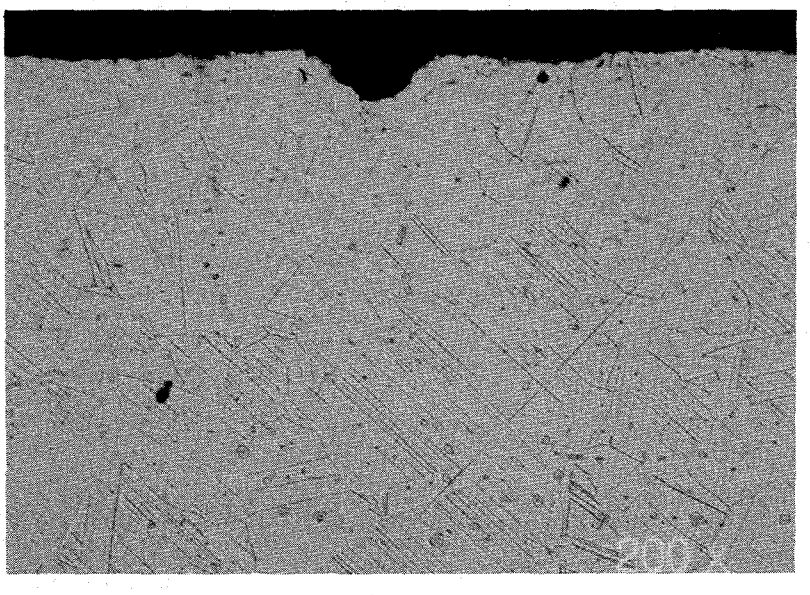
X 200

Fig. 6 Optical micrograph of cast steel after 1 year immersion in Q-brine at 90°C and a gamma dose rate of 10 Gy/h



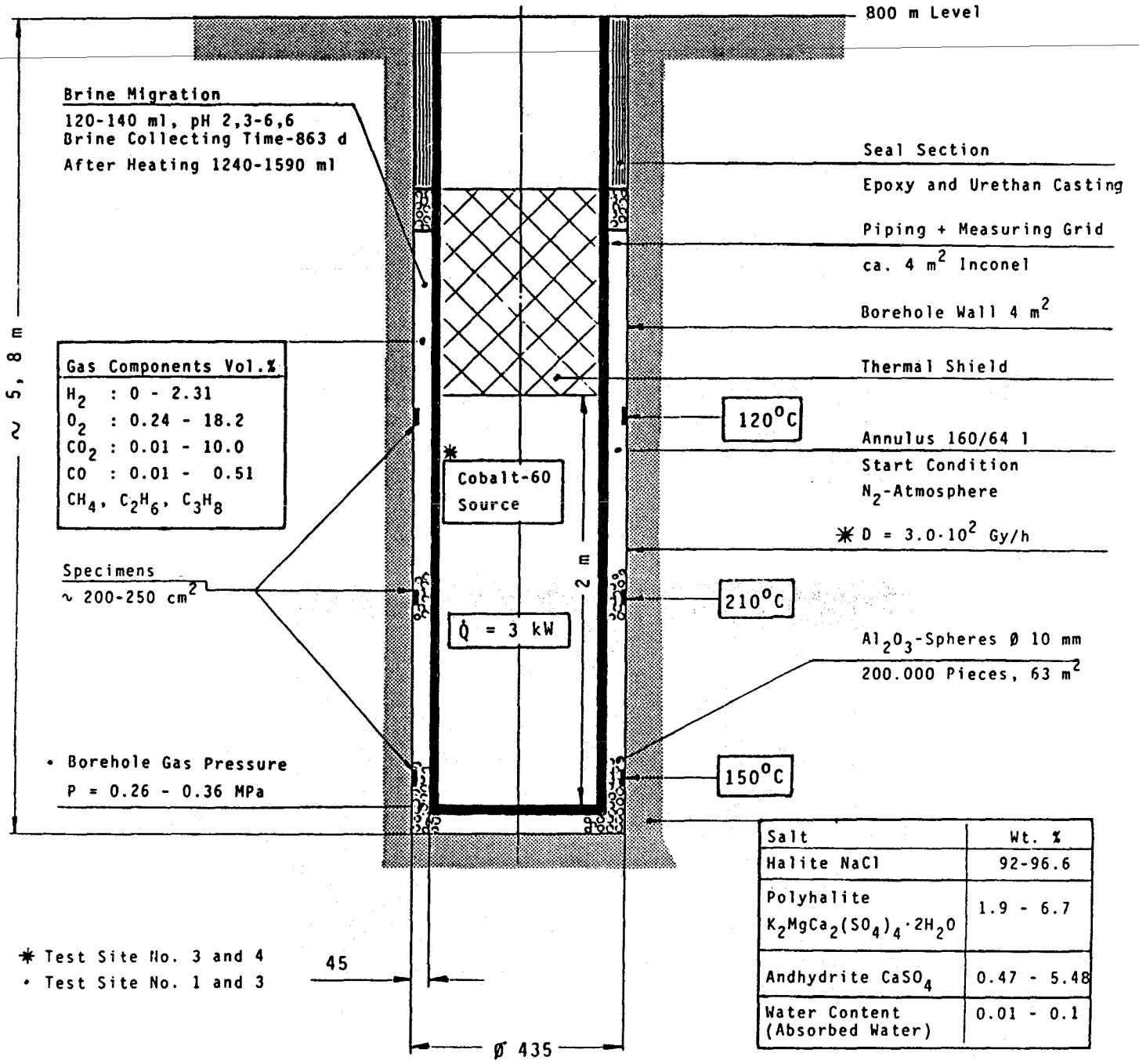
X 200

Fig. 7 Optical micrograph of Hastelloy C4 after 1 year immersion in Q-brine at 90°C and a gamma dose rate of 1 Gy/h



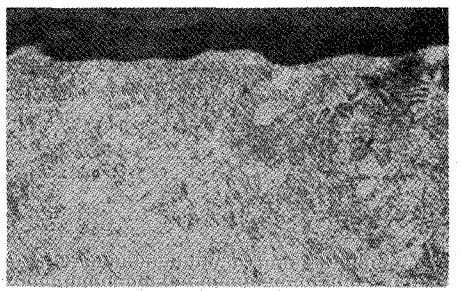
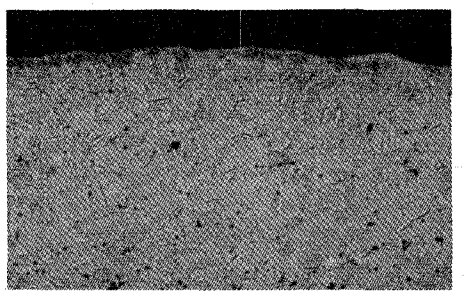
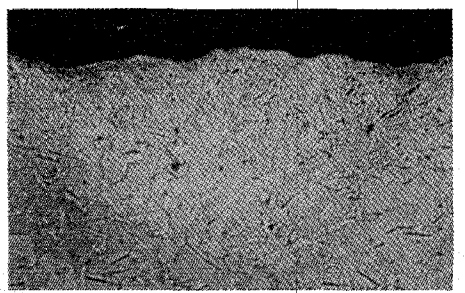
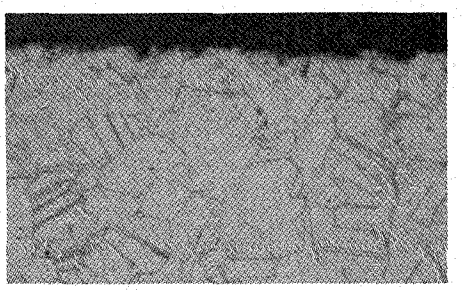
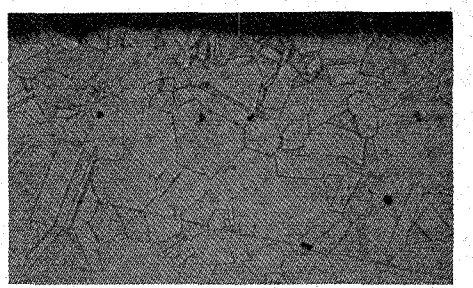
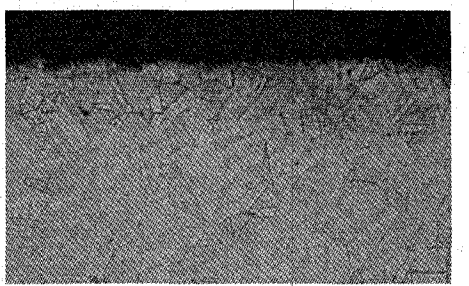
X 200

Fig. 8 Optical micrograph of Hastelloy C4 after 1 year immersion in Q-brine at 90°C and a gamma dose rate of 10 Gy/h



Salt	Wt. %
Halite NaCl	92-96.6
Polyhalite $K_2MgCa_2(SO_4)_4 \cdot 2H_2O$	1.9 - 6.7
Andhydrite $CaSO_4$	0.47 - 5.48
Water Content (Absorbed Water)	0.01 - 0.1

Fig. 9 Schematic Vertical Section of the Test Assembly with Indication of the Corrosion Conditions

MATERIAL	Before Exposure	After Exposure without Gamma-Irradiation T = 210°C, t = 900 d	After Exposure with Gamma-Irradiation T=210°C, t=700 d, $\dot{D}$ ca.$3 \cdot 10^2$ Gy/h
Ti 99.8-Pd			
Hastelloy C4			

0.1 mm 0.1 mm 0.1 mm

Fig. 10 Optical Micrograph of in situ - Corrosion Specimens

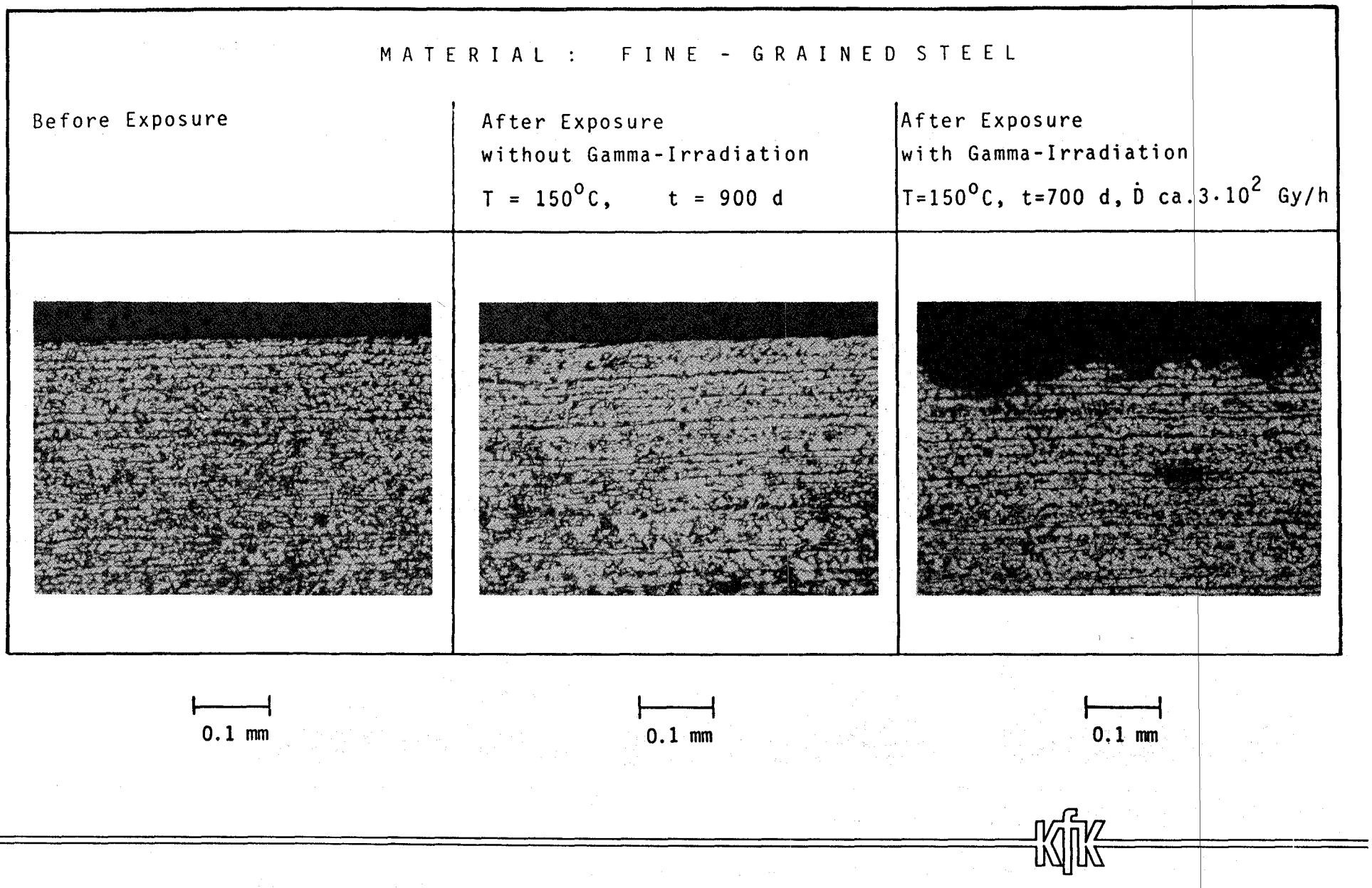


Fig. 11 Optical Micrograph of in situ - Corrosion Specimens

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