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United States Nuclear Regulatory Commission
Washington, D.C. 20555

Subject: Review of GPU Nuclear submissions on TMI-1 OTSGs to NRC, October 18/19, 1982, and of Battelle Columbus final report to GP Nuclear "Failure Analysis of Inconel 600 Tubes from OTSG A and B of Three Mile Island Unit-1."

Dear Mr. Benaroya:

I have reviewed the submissions of GPU Nuclear to NRC for rehabilitation of the TMI-1 OTSGs and the final report by Battelle Columbus to GPU Nuclear titled "Failure Analysis of Inconel 600 Tubes from OTSG A and B of Three Mile Island Unit 1." The submissions were made at a review meeting which was held at NRC in Bethesda October 18/19, 1982. A number of issues were raised during that meeting which I believe require careful analysis. My views on these issues are given below.

GPU Nuclear Submissions

1. Fatigue Crack Growth Rate Calculations.

GPU personnel presented the results of fracture mechanics calculations the fatigue crack growth rate in the Inconel 600 tubes as a result of flow-induced vibration. The computations made use of EPRI's "BIGIF" L.E.F.M. computational code, and a crack growth vs stress intensity range correlation for Inconel 600 that was apparently measured at MIT. It is immediately apparent upon examination of these calculations that the input data base is very tenuous. For example, the data used to derive the log (da/dN) vs log ΔK correlation were measured in pure water (although one point for PWR environments

was available) at an unrealistic R ratio (min. load/max. load = 0.05) and at a relatively high frequency (5 Hz). Although this frequency may be characteristic of flow-induced vibration, it is also likely that very low frequency (< 0.01 Hz) components are present due to load cycling. We will see later in this review that, in the case of sensitized Type 304 stainless steel (which is a reasonable model for "sensitized" I-600), the low frequency components lead to the most severe form of cracking. A further problem with the data is that it most likely refers to transgranular crack propagation (i.e., "mechanical" propagation) instead of environmentally-induced intergranular (IG) crack propagation. Note that the cracks that have been observed in the steam generators are intergranular in nature, although these cracks are believed to have propagated under near ambient conditions due to attack by polythionate species. The point is that IG propagation occurs in Type 304SS in high temperature solutions in the absence of polythionate species and it might also be expected to occur in sensitized I-600 in similar environments. If so, the data used by GPU in their fracture calculations may not be entirely appropriate.

Some other data exist for the propagation of cracks in I-600 in PWR primary environments. Data that have been obtained in this consultant's laboratory by Mr. Wen-ta Tsai (Graduate Student) are shown in Figures 1-5. Although these data were obtained at a more realistic R ratio (0.5) and over a range of frequency (10-0.1 Hz), the measurements were performed on mill-annealed material rather than on the sensitized state that exists in the TMI-1 OTSGs. Comparison of the GPU data with that given in Figures 1-5 shows that the two data sets are in reasonable agreement, which supports the contention that the MIT data may not refer to the metallurgical condition of the TMI OTSG I-600 tubes. Clearly, the data base used by GPU Nuclear requires further critical evaluation before the crack growth calculations can be taken as representative of what might be observed in the steam generators during operation. I recommend that the GPU calculations be repeated with "worst case" estimates for the crack propagation rate--possibly those for Type 304SS would be appropriate. Data for

sensitized Type 304SS are contained in the attached publication.

In their crack propagation analysis, GPU made a number of other assumptions which require critical examination. For example, they assumed that the damage mechanism has been arrested. This may or may not be the case, depending upon whether or not action is taken to remove sulfides from the surface. Also, they assume that "small cracks will not propagate mechanically." I agree that the danger of mechanical propagation (i.e., ductile or even transgranular fracture) is probably slight, and can be predicted with reasonable certainty using existing fatigue data. However, in my opinion, the greatest danger comes from the intergranular propagation which probably will occur even in the absence of polythionates given the metallurgical condition of the tubes. For reasons stated above (cf. data for Type 304SS), this type of crack propagation is likely to occur at low frequencies. I also have trouble with the assumption that "local IGA is acceptable." From a critical flaw viewpoint, it seems to me that a crack could very well propagate from "local IGA," provided that the flaw is sufficiently deep that the stress intensity exceeds the critical value for slow crack growth. In principle, it does not matter how the flaw is created--i.e., by IGSCC, IGA, or even by EDM--provided that the crack is sharp and that the right chemistry is established in the confines of the crack (this is likely to be the case for IGA). Given the extent of IGA detected by the Battelle failure analysis, I have very real reservations concerning the validity of this assumption.

2. Past ECT Examinations

GPU has invested a great deal of effort in developing eddy current testing (ECT) techniques for nondestructive examination of the steam generator tubes, and by-and-large this effort has been very successful. The sensitivity of the technique has been determined using machined notches which are thought to simulate cracks. While these calibrations may indeed define the sensitivity of the technique to straight flaws, no tests were apparently carried out to determine the sensitivity to highly branched cracks and in the extreme case to

IGA (Intergranular attack). GPU's response to questions concerning this matter was that IGA is not very prevalent in the steam generators. However, the recent final report from Battelle Columbus to GPU ("Failure Analysis of Inconel-600 Tubes from OTSG A and B of Three Mile Island Unit-1") notes the occurrence of IGA on many of the tubes examined. In many cases, grain decohesion was such that the grains had fallen out thereby resulting in pits.

A second point of some concern is the frequency of circumferential or near-circumferential cracks. The impression I gained during the meeting in Bethesda on October 18/19 was that the probability of circumferential or near-circumferential cracks existing in the tubes was sufficiently low that catastrophic tube fracture (i.e., complete fracture) could be ignored as a potential problem. However, the Battelle failure analyses on pulled OTSG tubes revealed the existence of a number of cracks that extended around a significant fraction of the tube circumference; some to the extent that fracture occurred during splitting of the tube for sample preparation. I believe that a careful analysis should be carried out on the distribution of cracks in terms of the number that occupy a given fraction of the circumference versus the circumferential distance. Because the probability of a tube break is likely to increase sharply with increasing circumferential length of a pre-existing flaw, I believe that such an analysis should be carried out by GPU using their own and the Battelle Columbus data in order to address this problem in a quantitative manner.

3. Future ECT Examinations

A great deal of time was spent at the Bethesda meeting debating whether or not additional ECT should be carried out after hot functional testing subsequent to completion of the SG repairs. GPU took the position that the risk of further damage to the SGs by exposing them to the atmosphere was not worth the possible gains. The purpose of the ECT would be to determine if any of the existing cracks had propagated further during the hot functional test or if any new cracks had nucleated. However, the precision of ECT is such

that I doubt if meaningful data could be obtained. Accordingly, I tend to agree with GPU's agreement that it would be far better to use fission product analyses on the secondary side to detect leaks. If leaks are detected, then it will be necessary to carry out a more detailed examination (presumably using ECT) to determine the locations of the leaking tubes. Of course, if no leaks are detected it cannot be concluded that existing cracks did not propagate, or that new cracks did not nucleate; only that the cracks did not penetrate the tube wall.

4. RCS Clean-up Activities

The effectiveness of the alkaline hydrogen peroxide method for desulfurizing sulfur-contaminated surfaces has been demonstrated, and some of the parameters that can be used to optimize the performance of the technique (e.g., stirring, temperature) have been identified.

Three options for the RCS clean-up activity were discussed by GPU personnel:

a) Desulfurize the steam generators only
b) Desulfurize the entire primary system
c) Desulfurize the primary system with the core removed.

It is my understanding that the entire primary system was contaminated by thiosulfate during the period 1979-1981, and hence it will be necessary to desulfurize the core as well as the steam generators. To my knowledge, zirconium alloys are not susceptible to sulfur attack or to attack by hydrogen peroxide, so that little danger probably exists of damage to the fuel elements themselves (this should be checked). However, other components, such as those fabricated from X-750 and Type 304SS may be susceptible, particularly if the components are in a sensitized metallurgical state. GPU is obviously concerned about this possibility, and is carrying out experiments in their corrosion program to address this issue. One other issue of minor concern is the copresence of H_2O_2 and IMUNOL in the system. My impression is that IMUNOL is an amine (or amide) of a long chain fatty

acid. If so, it is likely to be oxidized by hydrogen peroxide to produce degradation products such as nitrates, nitrites, and possibly nitrosamines. I believe that the principal effect may be that IMUNOL will compete with sulfur species for the available peroxide, and hence may reduce the effectiveness of the alkaline peroxide treatment for desulfurizing the system. Although some tests have been carried out by GPU and its contractors with both IMUNOL and H_2O_2 present at the same time, it is not clear if an interference really does exist. I believe that some additional testing may be called for if an interference is suspected.

One option that apparently has not been considered seriously is to generate H_2O_2 in situ under low power and in the absence of a hydrogen overpressure in the primary system. This would have the advantage that very minimal modifications would be necessary to the system, and that the desulfurization treatment could be carried out periodically if the situation so dictates.

5. Corrosion Program

GPU has initiated a corrosion program which is intended to detect any corrosion problems in the laboratory before they develop in the operating reactor. These tests employ both C-ring specimens and stressed SG tubes loaded in axial tension. These tests should prove to be effective, provided that the appropriate environments are tested. The tests proposed will use both uncontaminated and thiosulfate-contaminated PWR primary environments, as well as solutions containing H_2O_2 to simulate the desulfurization procedure. The thermal cycling proposed is realistic in terms of simulating hot functional testing and operational periods in the actual reactor. However, in a previous communication (letter of August 30, 1982) I expressed concern that no tests were being conducted (or apparently are planned) to simulate in situ regeneration of polythionic species by the oxidation of metal sulfides by oxygen during future cold shut down periods. Because no firm commitment has been made to desulfurize the primary circuit, I believe that it is essential to determine whether or not regeneration of the aggressive sulfur

species can occur and, if so, whether or not they will give rise to cracking of the tubes. Accordingly, I strongly recommend that NRC request that GPU carry out tests to simulate this scenario. An appropriate test might involve the following steps:

(a) Simulate cold-shutdown with thiosulfate and air contamination. Replace contaminated solution with uncontaminated boric acid.

(b) Simulate HFT and operating periods with H_2 over-pressure.

(c) Simulate second cold-shutdown with air contamination. Monitor for subsequent IGA and IGSCC.

Frequent chemical analyses should be conducted, particularly during period (c), to detect and quantify the formation of polythionic species due to metal sulfide oxidation. An effective method for detecting the presence of polythionic species, i.e., those species that can yield highly reactive elemental sulfur by dissociation, is to decompose them in acidic solution, extract the colloidal sulfur so formed with hexane, and then determine the intensity of absorption at γ = 250-500 nm in the visible/UV region of the spectrum. Calibration curves of log (I/I_o) versus concentration, where I and I_o are the transmitted light intensities for hexane with and without sulfur, respectively, thereby provide an analytical capability. I have attached a publication by Syrett, Macdonald, and Wing which describe this technique in more detail. Alternatively, ion chromatography may be used provided no interferences exist.

I also strongly recommend that the effectiveness of the peroxide desulfurization procedure be tested by repeating (a) through (c), but with a peroxide soak after step (b) followed by a boric acid rinse. I believe that the tests outlined above would effectively address the issue as to whether or not polythionic species can form by the oxidation of metal sulfides during subsequent cold shutdown periods during which air has been admitted to the system.

Battelle Columbus Report

The final report "Failure Analysis of Inconel 600 Tubes from OTSG A and B of Three Mile Island Unit-1" submitted to GPU-Nuclear by Battelle Columbus Laboratories on June 30, 1982, describes a comprehensive analysis of a number of Inconel 600 tubes which were pulled from the TMI-1 OTSGs. The analyses performed included metallography and microstructural examination, ECT, microanalytical surface examination, and physical tests (e.g., microhardness). The microanalytical techniques used included SEM-EDAX, Auger spectroscopy, ESCA, and SIMS. Corrosion products were also identified using X-ray diffraction techniques, and the susceptibility of a few tubes to IGA by polythionic attack was determined using the electrochemical potentiokinetic reactivation (EPR) technique. Some X-ray isotopic analyses were carried out to identify the active isotopes present in the secondary system.

The physical examinations demonstrated the existence of numerous cracks, many of which had penetrated the tube walls, as well as regions of IGA. Although most of the cracks occupy less than 50° of arc, a number apparently extended for more than 180° of arc, and hence can be classified as "near circumferential" in nature. For reasons discussed in the previous section, quantitative data for the distribution in crack length would be extremely valuable for assessing the probability of catastrophic fracture of tubes in service. Unfortunately, the required data were not obtained, either because the population of cracks was too small to generate a statistically meaningful distribution or because the need for this information was not perceived by the authors.

It is interesting to note that the authors concluded that "no continuous network of carbides was observed in any tube, thus, indicating no severe sensitization." However, I do not believe that this conclusion is bourne out by the microstructural examinations reported in their study. For example, the micrographs shown in Figure 42 show extensive intergranular (grain boundary) and intragranular carbide precipitates, with those along the grain boundaries being "continuous" or very nearly so and typical of severely-sensitized

microstructures. The severity of sensitization is also clearly shown by the EPR test data.

The conclusion that corrosion fatigue can be ruled out as a failure mode because striations were not observed on the fracture surfaces should also be made with caution. Fatigue striations frequently appear at relatively high frequencies, particularly if failure occurs in a transgranular mode. Experience with corrosion fatigue in Type 304SS in high temperature solutions (see attached preprint) shows that striations are only rarely observed on intergranular facets which result from fracture at low frequencies (< 0.1 Hz).

The high levels of carbon observed in the corrosion product film is also very interesting. Similar observations have been made on copper-nickel alloys in sea-water, and no ready explanation exists for this particular case. However, the explanation provided by the authors, i.e., prior oil contamination, is probably correct particularly in view of the fact that the carbon was in the graphitic or long chain hydrocarbon form.

I concur, generally, with the failure scenario proposed by the Battelle workers, with one exception. They assume that, because the sulfur detected on the tubes is primarily in the form of sulfide (NiS or Ni_2S_3), the sulfur compounds present in the OTSGs were reduced to sulfur or sulfide at high temperatures in the presence of hydrogen during the hot functional. The reduced forms are then considered to react with the metal to form metal sulfides. However, thiosulfate already contains zero-valent sulfur (i.e., $S \cdot SO_3^{2-}$) and hence can react directly with iron and nickel to form metal sulfides

$$M + S_2O_3^{2-} \rightarrow MS + SO_3^{2-}$$

Thus, a prior hot functional is not necessary as the claim by Battelle would imply.

If you have any questions concerning my review please call me at (614) 422-6255 at your convenience.

Yours sincerely,

D. D. Macdonald

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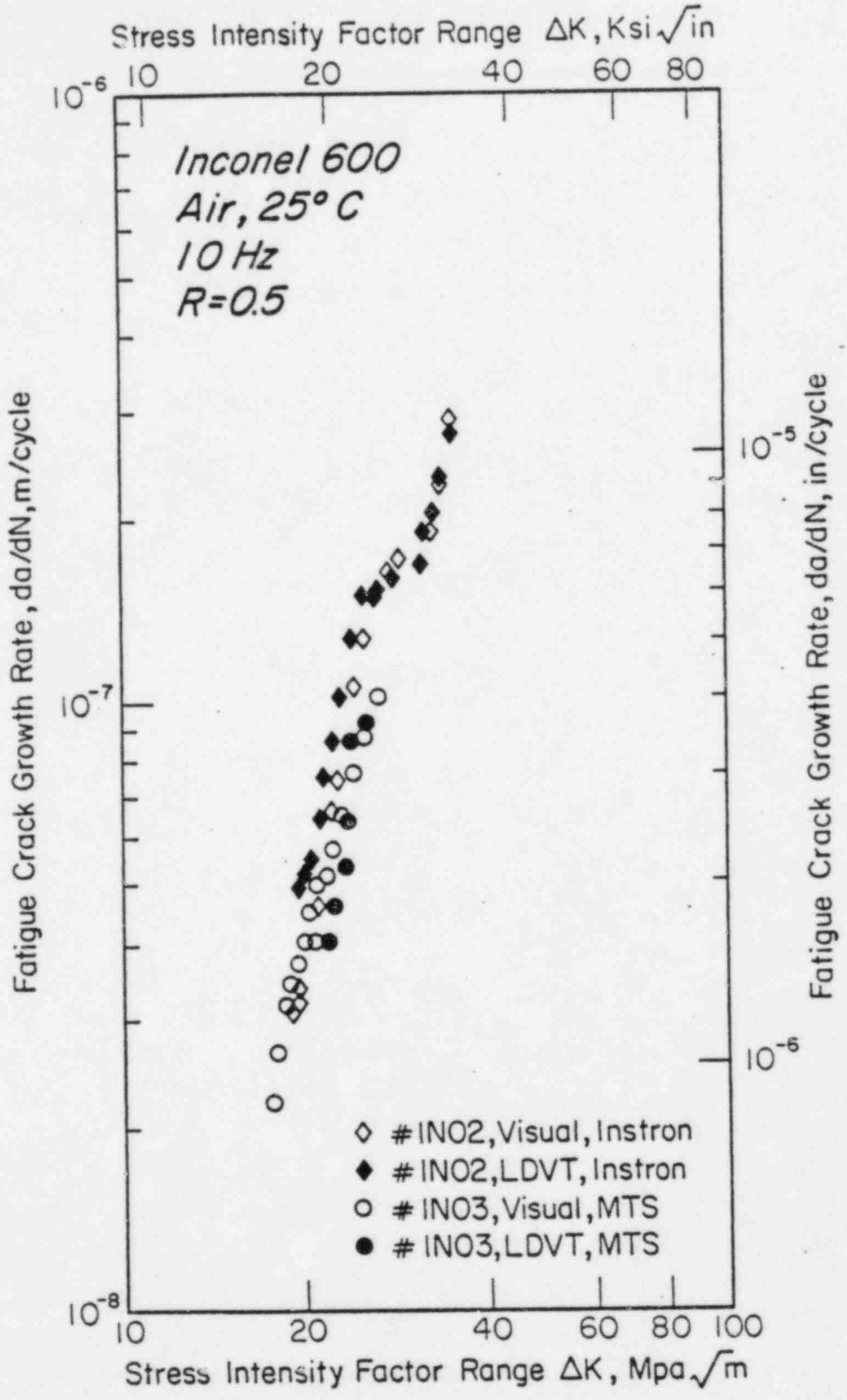

Stress Intensity Factor Range ΔK, Ksi √in
10
20
40
60
80
Inconel 600
Air, 25° C
10 Hz
R=0.5
10^-6
10^-7
10^-8
Fatigue Crack Growth Rate, da/dN, m/cycle
10^-5
10^-6
Fatigue Crack Growth Rate, da/dN, in/cycle
◇ #IN02, Visual, Instron
◆ #IN02, LDVT, Instron
○ #IN03, Visual, MTS
● #IN03, LDVT, MTS
10
20
40
60
80
100
Stress Intensity Factor Range ΔK, Mpa √m

Fig. 1

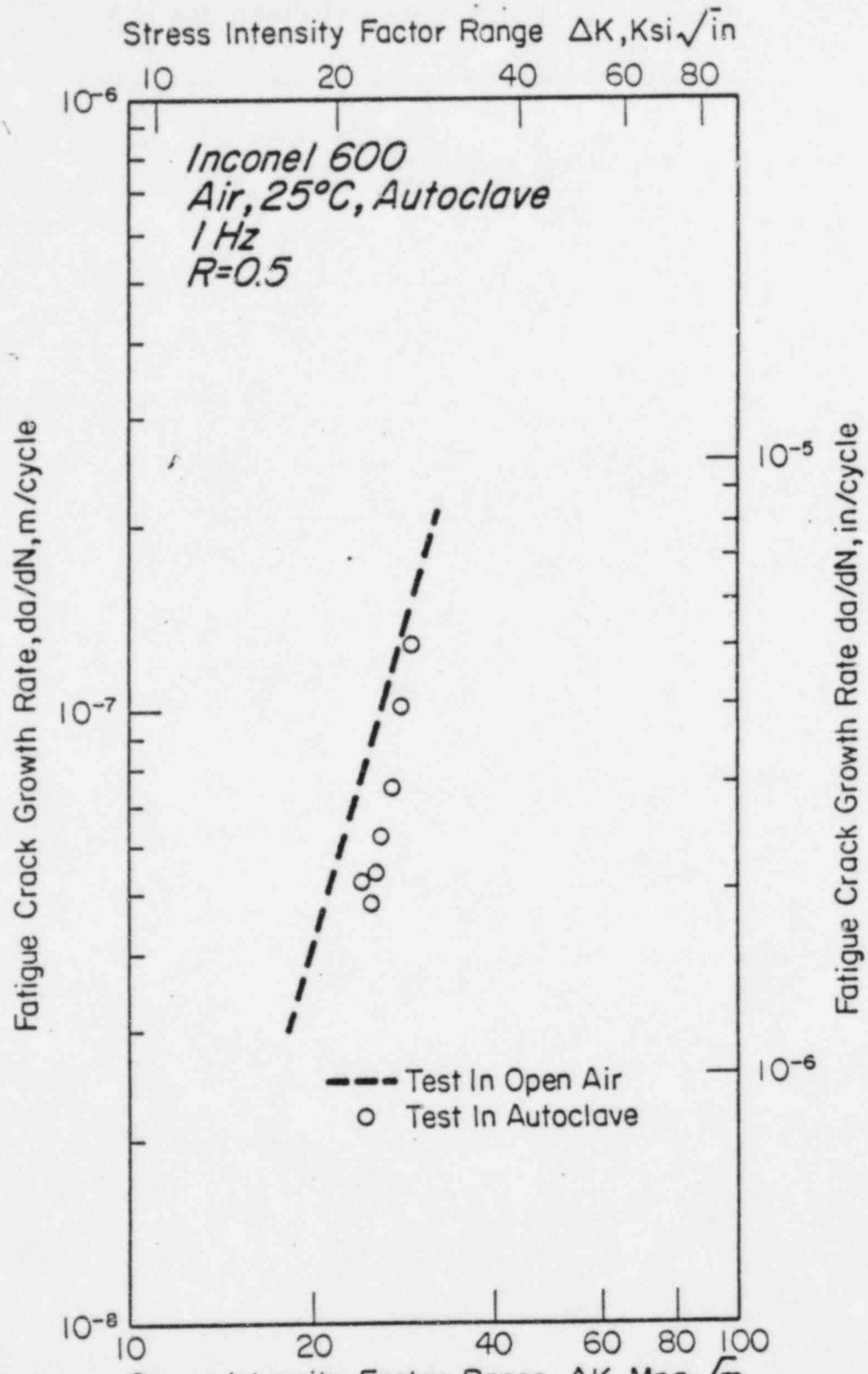
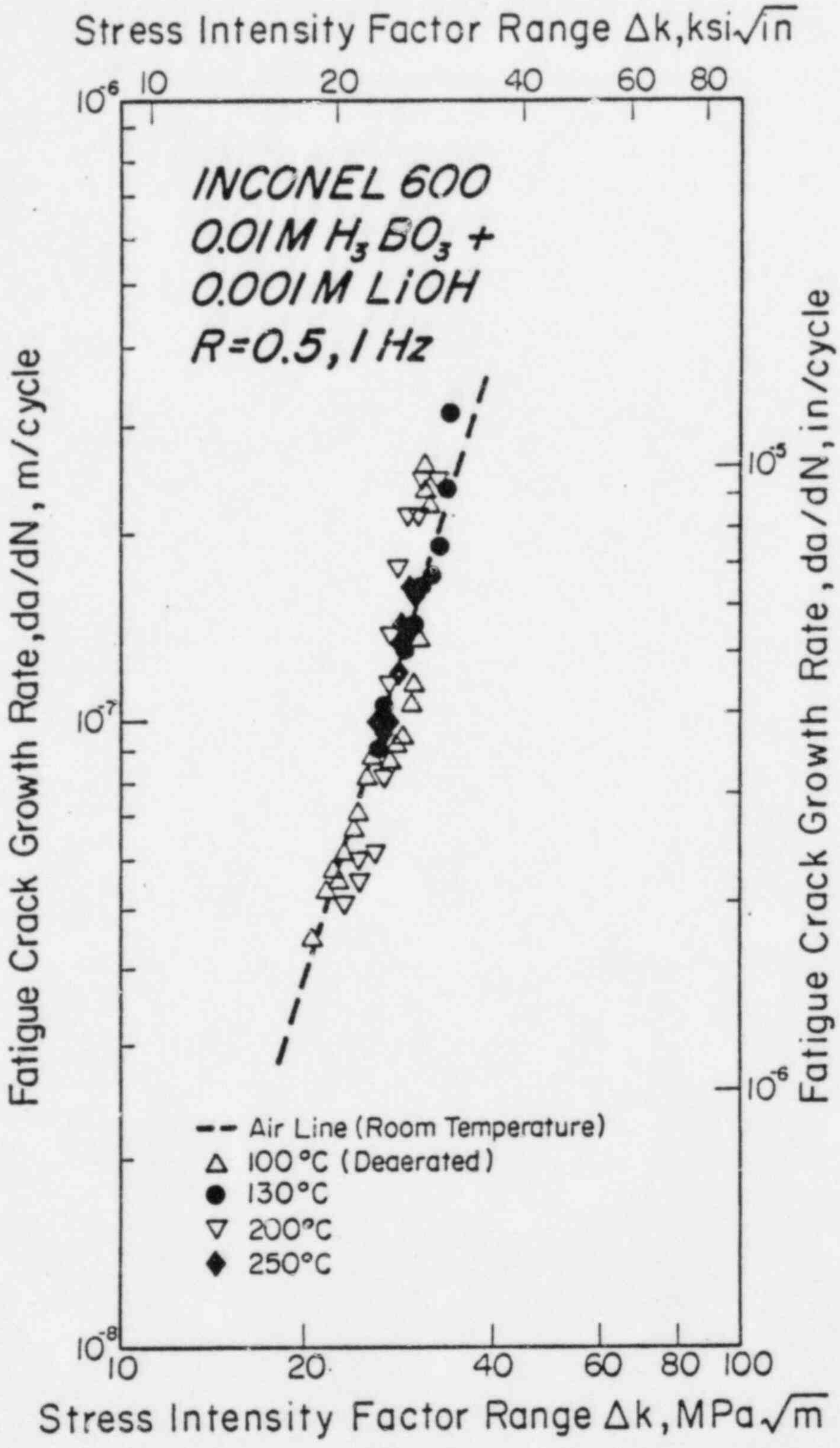

Stress Intensity Factor Range ΔK, Ksi√in
10
20
40
60
80
10^{-6}
Inconel 600
Air, 25°C, Autoclave
1 Hz
R=0.5
10^{-5}
10^{-7}
10^{-6}
Test In Open Air
Test In Autoclave
10^{-8}
10
20
40
60
80
100
Stress Intensity Factor Range ΔK, Mpa√m
Fatigue Crack Growth Rate, da/dN, m/cycle
Fatigue Crack Growth Rate da/dN, in/cycle

Fig. 2



Stress Intensity Factor Range Δk, ksi√in
10
20
40
60
80
INCONEL 600
0.01 M H3BO3 +
0.001 M LiOH
R=0.5, 1 Hz
Fatigue Crack Growth Rate, da/dN, m/cycle
Fatigue Crack Growth Rate, da/dN, in/cycle
10^-6
10^-7
10^-8
10^-5
10^-6
Air Line (Room Temperature)
100°C (Deaerated)
130°C
200°C
250°C
10
20
40
60
80
100
Stress Intensity Factor Range Δk, MPa√m

Fig. 3

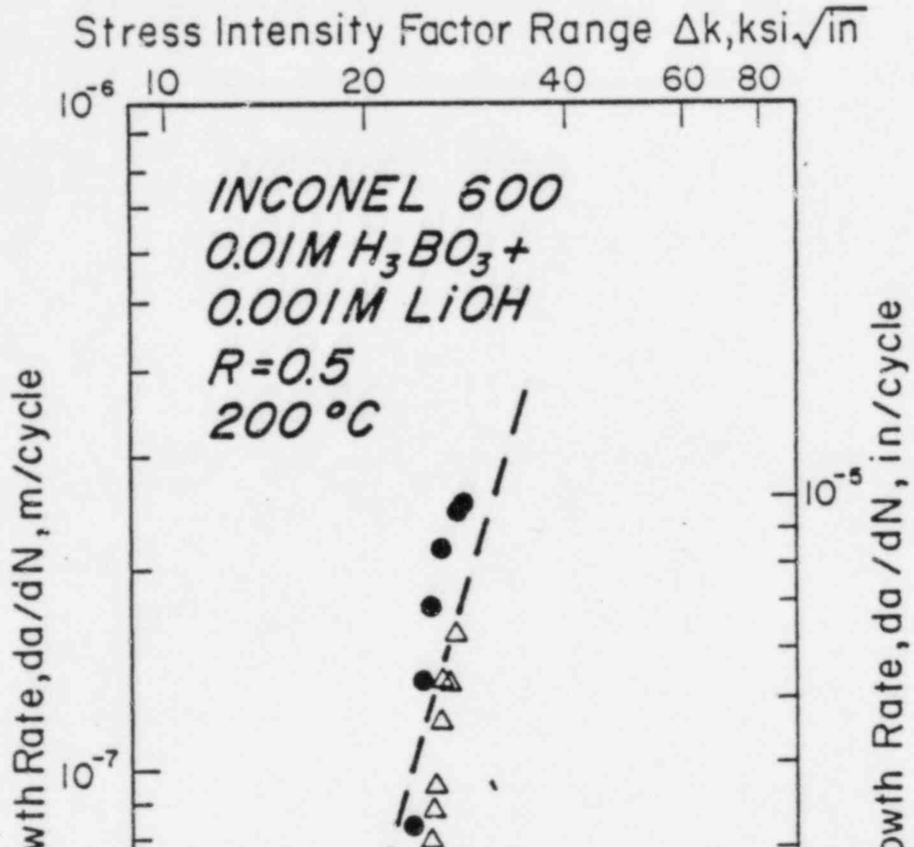

Stress Intensity Factor Range Δk, ksi√in
10
20
40
60
80
INCONEL 600
0.01M H_3BO_3 +
0.001M LiOH
R=0.5
200 °C
Fatigue Crack Growth Rate, da/dN, m/cycle
Fatigue Crack Growth Rate, da/dN, in/cycle
10^{-6}
10^{-7}
10^{-8}
10^{-5}
10^{-6}
-- Air Line (Room Temperature)
● 1 Hz
△ 0.1 Hz
10
20
40
60
80
100
Stress Intensity Factor Range Δk, MPa√m

Fig. 4

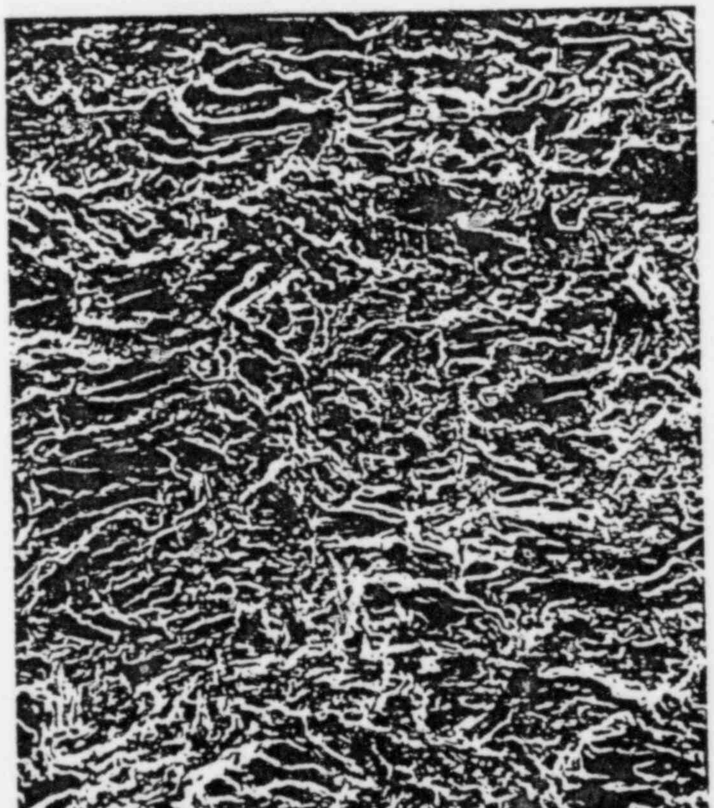


Fig. 5 [illegible]