WATER CHEMISTRY AND MATERIALS DEGRADATION IN LWR'S

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ABSTRACT. Water chemistry plays a major role in corrosion, in erosion corrosion and in activity transport in NPP's. Although a full understanding of all mechanisms involved in corrosion does not exist, controlling of the water chemistry has achieved good results in recent years. Water chemistry impacts upon the operational safety of LWR's in two main ways:

- integrity of pressure boundary materials and
- activity transport and out-of-core radiation fields.

Good control of water chemistry can significantly reduce the above mentioned problems and hence improve plant safety. However, economic pressures are leading to more rigorous operating conditions in power reactors. Fuel burnups are to be increased, higher efficiencies are to be achieved by running at higher temperatures and plant lifetimes are to be extended.

This paper will describe application of water chemistry control in operating reactors to prevent corrosion. It will also give an overview on some problems experienced in LWR's operating at high temperatures. These experiences should be periodically reviewed in order to improve the operational safety and extend the life time of the nuclear power plants.

Keywords: Water chemistry, corrosion, erosion, activity transport, plant safety, life time extension, light water reactors

1 INTRODUCTION

The IAEA co-ordinate research program entitled "Investigation on Water Chemistry Control and Coolant Interaction with Fuel and Primary Circuit Materials in Water Cooled Power Reactors (WACOLIN)" was organized and carried out from 1987 to 1991. The reports of this work summarize the present understanding on good coolant chemistry (IAEA Technical Reports Series No. 347 and IAEA-TECDOC-667):

"Good reactor coolant chemistry, corrosion control and minimum of activity build-up are indispensable for the optimum performance of nuclear power plants. Without these the system integrity may be jeopardized and the activity transport may create various problems".

For a nuclear power plant the capability to operate with an optimal chemistry regime is determined by the design including materials, construction and effectiveness of the water purification system. The choice of materials defines water quality requirements and dimensions of water treatment systems. Some features of design like the use of copper-base alloys or Inconels or carbon steels presents limitations for the optimum water chemistry. Therefore recommendations for water chemistry must be established together with the design and material specifications.

Reliable water chemistry specifications have been developed for the existing water cooled reactors taking into account the common material practice for high temperature operation; however, there is still room for improvement. Water cooled power reactor experience shows that even under normal operating conditions some undesirable phenomena can occur like stress corrosion cracking and corrosion fatigue, erosion corrosion or deposition of corrosion products on heat transfer surfaces. Therefore, more stringent control of water chemistry during plant operation, eventually through on-line monitoring (Aaltonen et al. 1992), should be implemented.

2 PWR COOLANT

The goal of recommendations for chemistry in operating PWR's is to limit radioactive transport and thereby reduce out-of-reactor radiation fields. Radiolytic oxygen formation in PWR's is suppressed by maintaining an overpressure of hydrogen. Generally 25 - 30 cc/kg are required to keep oxygen below 5 ppb. Control of pH in PWR primary systems is complicated by the use of boric acid as a chemical shim to control nuclear reactivity, which results in a need to adjust lithium or potassium hydroxide content to avoid a continually changing pH through the fuel cycle.

Typical water chemistry specifications used in PWR's are shown in Tables 1 and 2 as well as in Fig. 1. The three options being consistent with the guidelines are:
- Elevated Li-B-Chemistry
- Modified Li-B-Chemistry
- Co-ordinate Li-B-Chemistry.

The operational experience of the last years has shown that the modified Li-B-Chemistry should be preferred over the other two options. Corrosion product transport and solubility has been lowest and the estimated relative activity build-up on cold regions of the primary circuit, as a result of precipitation and activation on hot regions and subsequent dissolution and redistribution throughout the system, is minimized (Rieβ 1993).

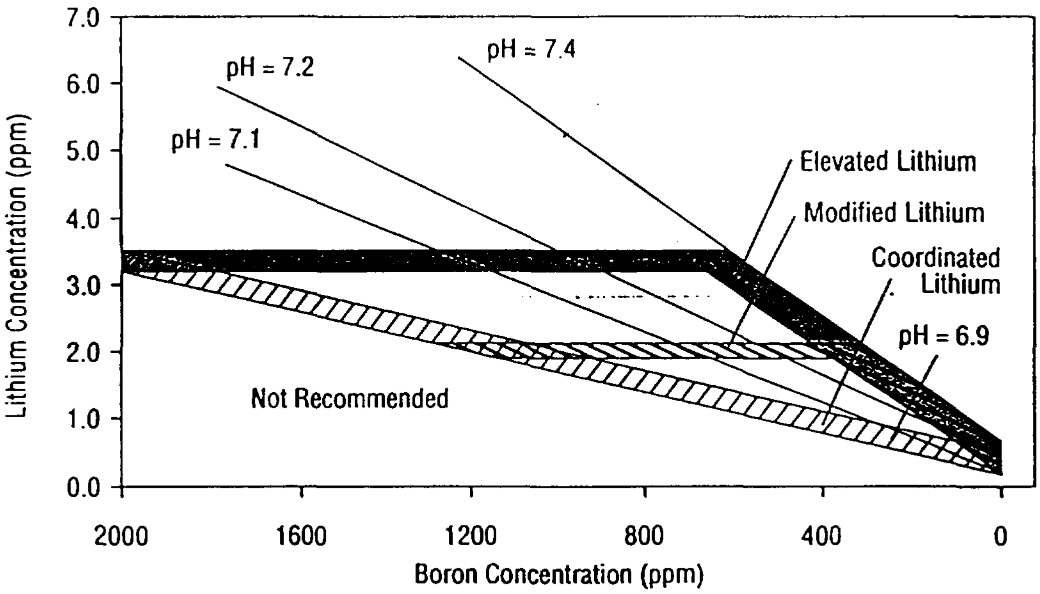

Fig. 1. PWR primary system chemistry control regimes (EPRI NP-7077 1990).

PWR primary water chemistry changes greatly at shut-down, when the coolant is oxygenated and borated during cooling period. This change will release activated corrosion products which can be collected by clean-up systems operating at full power.

The guidelines give a possibility to great variation especially concerning pH optimization. This optimization must be done plant-specific. Generic principles for optimization of primary system pH are presented in EPRI Guidelines (EPRI NP-7077 1990), like shown in Fig. 2.

Table 1. EPRI guidelines for primary coolant in PWR's (EPRI NP-7077 1990).

Hydrogen (cm^3) (STP)/kg H_2O [a]	25 - 50
chlorides (mg/kg)	< 0.15
fluorides (mg/kg)	< 0.15
dissolved oxygen (mg/kg)	< 0.01
lithium (mg/kg)	consistent with station lithium program

[a] STP, standard temperature and pressure (0°C, atm)

Table 2. Specifications of reactor water quality for PWR's of VVER-440 and VVER-1000 type (Rieß 1993).

Control parameter	Values VVER-440	 VVER-1000
pH (25°C)	6.0 - 10.2	5.7 - 10.2
K^+, L^+, N^+ (mmol/kg) (depending on H_3BO_3 concentration)	0.05 - 0.45	0.05 - 0.45
NH_3 (mg/kg)	> 5.0	> 5.0
hydrogen (cm^3/kg)	30 - 60	30 - 60
chlorides and fluorides (µg/kg)	≤ 100	≤ 100
H_3BO_3 (g/kg)	0 - 9.0	0 - 13.5
oxygen (µg/kg)	≤ 5	≤ 5
copper (ng/kg)	< 20	< 20
iron (ng/kg)	< 200	< 200

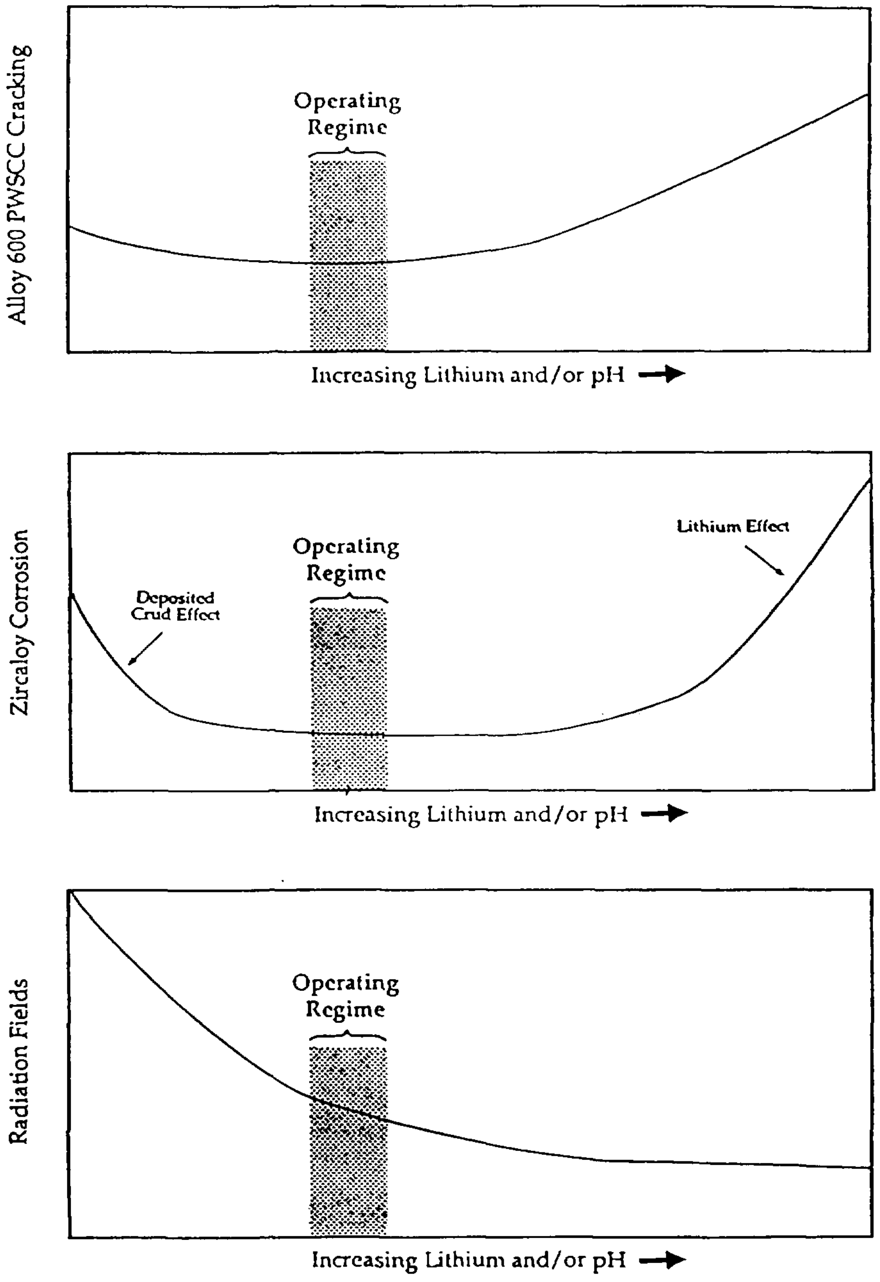

Fig. 2. Schematic presentation of the PWR primary chemistry optimization problem (EPRI NP-7077 1990).

3 BWR COOLANT

BWR's operate under constant oxygen chemistry throughout the fuel cycle and so there is no changes taking place like in PWR's during shut-down affecting the transport of activated corrosion products. Thus, the deposition rate of activity is mainly controlled by the corrosion rate during steady state operation. The aim of the BWR water chemistry is to control the corrosion product input in the feedwater, to reduce crud build-up and to control and minimize radiation field build-up on recirculation piping. Both the above aspects of BWR radiation control require that feedwater and reactor water are kept as pure as possible (EPRI NP-4946-SR 1988).

BWR water chemistry specifications according to the EPRI guidelines are listed in Table 4. These and corresponding guidelines are now worldwide under review. The existing operational problems, specially the IGSCC problem, require more stringent values. For example, it is currently discussed to fix the chlorides and sulphate values of the reactor water for action level 1 at 5 ppb. Also, the iron level of the feedwater seems to be too high. BWR water chemistry has also been modified in order to moderate the SCC problems. Hydrogen water chemistry (HWC) has been used to control intergranular stress *corrosion cracking. However, applied HWC has resulted in two radiation effects. The first* effect is the increase in N-16 radiation. The second is the Co-60 shut-down radiation field mainly caused by a similar change in the redox environment like in PWR chemistry. Zinc injection has been studied in consideration for reducing cobalt-60 fields. Noble-metal coatings (Pt, Pd) or noble metals as an alloying element have been demonstrated to improve the effects of hydrogen water chemistry. Noble metals even at low concentrations enhance the cathodic reactions and, thus, decrease of corrosion potential takes place faster when hydrogen is induced.

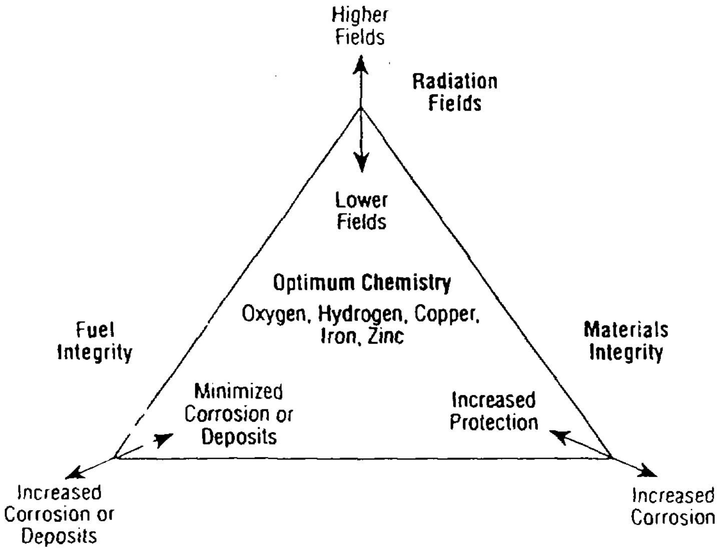

Fig. 3. Problems with optimizing BWR chemistry (EPRI TR-100265 1992).

Table 4a. EPRI water chemistry guidelines for BWR's (EPRI NP-4946-SR 1988).

Control parameter	Frequency of measurement	Achievable value	Action levels 1	2	3
Reactor water during power operation					
Conductivity (µS/cm at 25°C)	continuously	≤0.20	>0.30	>1.0	>5.0
Chloride (ppb)	daily	≤15	>20	>100	>200
Sulphate (ppb)	daily	≤15	>20	>100	>200
Diagnostic parameter, silica (ppb)	daily	≤100			

Table 4b. EPRI water chemistry guidelines for BWR's (cont'd) (EPRI NP-4946-SR 1988).

Control parameter	Frequency of measurement	Achievable value	Action levels 1	2	3
Reactor feedwater / condensate during power operation					
Feedwater conductivity (µS/cm at 25°C)	continuously	≤0.06	>0.07		
Condensate conductivity	continuously	≤0.08	>0.10		>10
Feedwater total copper (ppb)	weekly integrated	≤0.10 ≤0.30	>0.50 >0.50		
Feedwater total iron (ppb)	weekly integrated	≤2.0	>5.0		
Feedwater dissolved oxygen (ppb)	continuously	20-50	<10 >200		

4 ENVIRONMENTALLY ASSISTED CRACKING (EAC) IN LIGHT WATER REACTORS (LWR'S)

Environmentally assisted cracking of LWR pressure boundary components has caused significant outages with occasional safety hazards. Most of the components of nuclear power plants have been affected by corrosion damage. Environment sensitive cracking incidents in pressure vessels, piping and heat exchanger have led to replacements of these major components often after only a small fraction of their design life. Numerous reviews of environment sensitive cracking in light water reactor components have been presented (e.g. Stahlkopf 1982, Berry 1984, Scott 1985, Norring & Rosborg 1984, Hänninen & Aho-Mantila 1985, Hänninen & Aho-Mantila 1986, Hänninen, Aho-Mantila & Törrönen 1987).

The complex interplay of metallurgical, mechanical and environmental factors in environment sensitive cracking is shown in Fig. 4. The number of variables that affect environment sensitive cracking in light water reactor conditions is large and they possibly have a number of synergistic interactions.

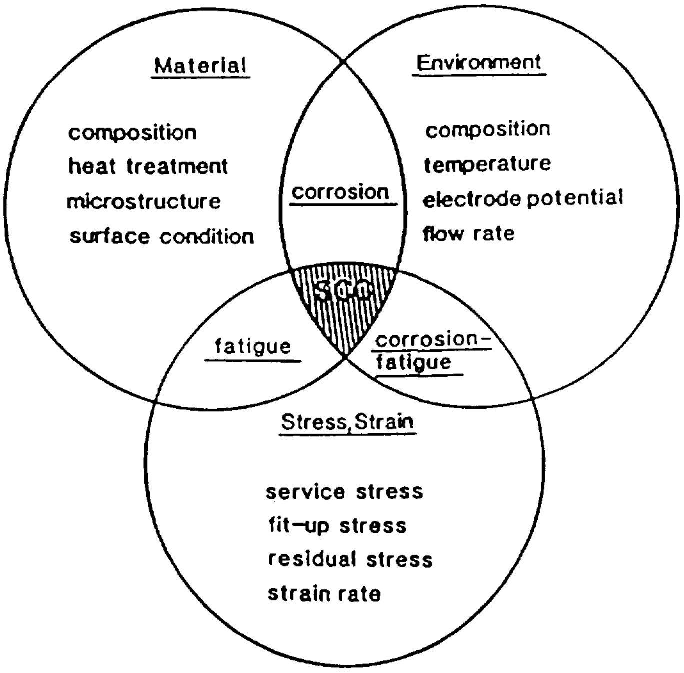

Fig. 4. Factors affecting environment sensitive cracking. Note that specific conditions are required for cracking to occur.

4.1 Carbon steels

Corrosion fatigue is the main problem associated with carbon steels in LWR's. The environment sensitive cracking properties of pressure vessel steels such as A533B and A508 have been studied to a large extent. Appendix A of Section XI of the ASME Boiler and Pressure Vessel Code presents a procedure for estimating the remaining useful life of a cracked reactor pressure vessel or nozzle. This procedure combines a fatigue crack growth analysis with a maximum allowable flaw size. Results obtained in PWR conditions lie usually below the ASME curves (see e.g. Cullen, 1985 & 1986). However, results obtained in pure water containing high dissolved oxygen contents indicate considerably higher crack growth rates than the ASME reference curves, Fig. 5.

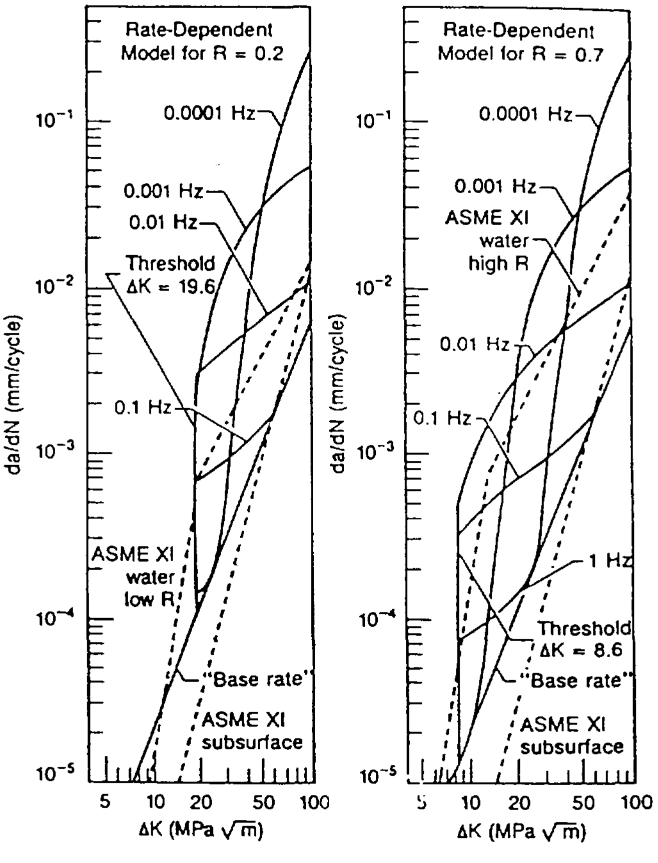

Fig. 5. Predictive curves based on time-dependent corrosion fatigue crack growth model for reactor pressure vessel steels in reactor grade water at 288°C (Gilman 1986).

The importance of metallurgical variables of steels is now clear, based on the laboratory test results. The sulphur content and, especially, the MnS inclusion size, shape and distribution in the steel seem to be responsible for material-to-material and heat-to-heat variability. Large elongated MnS inclusions generally contribute to rapid crack growth rates, whereas materials containing small spherical MnS inclusions are less susceptible. The sulphur species produced from the dissolution (H_2S, HS^- etc.) are known both to enhance hydrogen absorption and to increase anodic dissolution of the steel.

Besides the reactor vessels there has also been cracking in uncladded steam generator shells of PWR's, in steam generator feedwater piping of PWR's, in carbon steel piping of BWR's and in feedwater tanks of nuclear reactors, which are mechanistically relevant to pressure vessel steel problems.

Thermal fatigue is the primary cause of steam generator feedwater pipe cracking incidents induced by thermal stratification during low flow conditions during plant start-up and low power operation. Cracks are oriented circumferential and located in the base metal outside the weld heat-affected zone. Pitting was associated with the initiation of the cracks. Temperature differences of the order of 120°C have been measured from feedwater lines between the top and the bottom under low flow conditions. The main factor affecting this cracking is thought to be the large number of thermal stratification cycles (0.1-10 Hz); the feedwater chemistry, particularly the oxygen level, was of secondary concern. However, they both contribute significantly to crack initiation.

Strain-induced corrosion cracking (SICC) has caused cracks in the medium-strength, low alloy steel 17MnMoV64 and in the relatively high-strength, fine-grained, structural steel 22NiMoCr37 used in Germany for BWR piping and reactor vessel nozzles. This kind of cracking has caused circumferential cracking in the region of feedwater nozzles and at welds and axial cracking in pipe bends, but also cracking in straight sections of thin-walled piping in German BWRs. SICC refers to those corrosion situations in which the presence of localized, dynamic straining is essential for crack formation to occur, but in which cyclic loading is either absent or is restricted to a very low number of infrequent events. The high content of dissolved oxygen seems to be an important factor. Oxygen leads to the formation of mixed magnetite/hematite oxide films on low-alloy steel surfaces.

Erosion-corrosion has reduced pipe wall thickness in several PWR's. An oxide dissolution mechanism is believed to be the mechanism of erosion-corrosion. The interaction of piping design, flow velocity (5 ms^{-1}), temperature and pressure (193°C/25 bar), pH (8.8-9.2), unusually low amounts of alloying elements of the steel, particularly chromium (less than 0.02 %) as well as extremely low oxygen content (less than 4 ppb) in the water, contribute to this type of degradation (Bignold et al. 1980, Heitmann and Schub 1983). The findings concerning erosion corrosion have been summarized in Fig.6. Even materials chemical composition does not provide erosion corrosion resistance it can be supported by application of appropriate water chemistry parameters. Generally, this type of corrosion has been a problem on the secondary loop materials. Erosion-corrosion may become an increasing problem in BWR's with carbon steel feed water lines, if the water chemistry is changed to a hydrogen water chemistry (HWC).

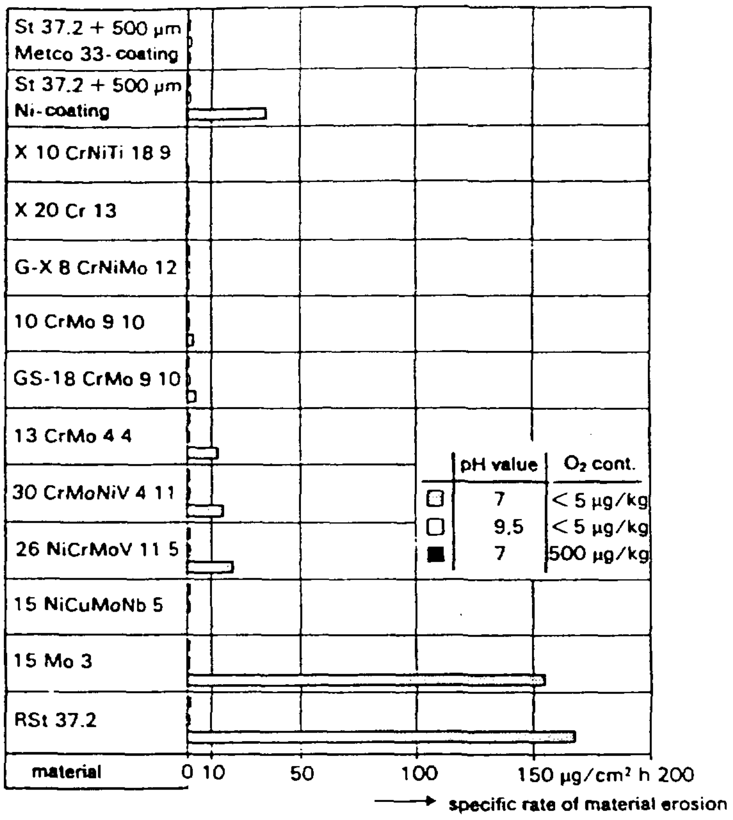

Fig. 6. Material erosion by corrosion/erosion on different materials.
p = 40 bar, T = 180°C, v = 29 m/s (Dörr, Odar & Schub 1986).

4.2 Stainless steels and nickel base alloys

Intergranular stress corrosion cracking (IGSCC) in the weld heat affected zones (HAZ) of AISI 304 and 316 stainless steel reactor pressure vessel nozzle safe-ends and piping have occurred in several BWR's. The BWR pipe cracking has occurred in the sensitized zones of AISI 304 and 316 type stainless steel weldments. After welding the degree of sensitization is generally low, but it can increase during operation due to low temperature sensitization (LTS). The development of a sensitized microstructure in LTS as a function of time is shown in Fig. 7. It can be seen that in about 10 years a marked change in the weld sensitized structure can be expected at reactor operating temperatures. Also welded stabilized stainless steels have suffered from SCC in BWR's. Localized yielding due to reduced wall thickness and changes in microstructure caused by the welding have made materials susceptible to SCC.

In addition to the sensitized microstructure and stresses the presence of a certain amount of oxygen in the coolant is necessary for BWR IGSCC. In general, by keeping the amount of oxygen in the coolant low enough IGSCC is inhibited, but the exact level depends on the conductivity of the water. To prevent crack formation in BWR stainless steel piping the electrochemical potential in the cooling water has to be kept more negative than about -250 mV_{SHE}. Under normal conditions of 100 - 300 ppb dissolved oxygen the electrochemical potential in BWR water varies from plant to plant between -100 and +100 mV_{SHE} which supports stress corrosion cracking. If the conductivity of the water is below 0.3 $\mu S\ cm^{-1}$, the 20 ppb of oxygen is sufficient low to keep the potential on the right level and to inhibit IGSCC. Therefore, hydrogen addition in conjunction with impurity control has become into widespread use in BWR practice for preventing and mitigating cracking in piping.

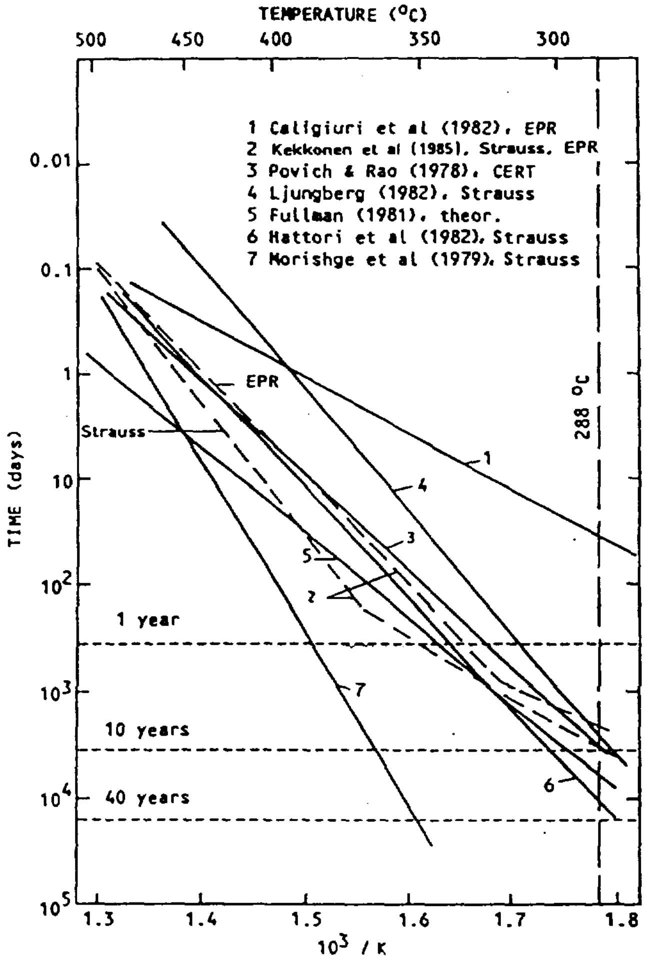

Fig. 7. Several (T, t) dependencies for LTS of AISI 304 steel showing wide scatter of various tests. The scatter is based on the various starting conditions used as well as test methods (Kekkonen et al. 1985).

Cold work and residual stresses has been attributed to a number of AISI 304 steel pipe cracking incidents in BWR's. Cracking in these cases can be mainly intergranular. An example of this type of cracking has occurred in AISI 304 elbows in the shut-down cooling and clean-up system in a BWR plant. In cold bending the inner surface deformation (15-20 %) produced some α'-martensite, which initiated axial cracking in the pipe bend in the absence of sensitization.

IGSCC of Inconel 600 has been detected e.g. in a recirculation inlet nozzle safe-end weld. The safe-ends were made of Inconel 600 forging and all safe-ends of the plant showed cracking essentially completely around the circumference. Cracking had initiated in the weld HAZ and propagated through the safe-end weldment (Inconel 182). This plant had marked resin intrusions which lowered the pH and increased the conductivity. A large number of recent cracking cases of Inconel 182 weld metal in BWR's emphasizes especially the need for good water quality control. In PWR's similar cracking incidents concerning Inconel 600 and Inconel 182 used in the pressure vessel head penetrations have been observed in many plants.

Thermal fatigue cracks accounts for only a small percentage of the total pipe cracks in stainless steel piping if compared to IGSCC. These cracks are transgranular and can be prevented by modifying the pipe system design and installing mixers to minimize the thermal gradients. These cracks may be a problem in areas which do not belong to current in-service inspection programs and, thus, for early identification of leaks a good leak detection system is important.

In stagnant borated water of PWR's a number of cracking incidents have been reported. Cracking has occurred in low pressure systems in the heat-affected zones of AISI 304 stainless steel pipe welds but also in the cast stabilized stainless steel components. Investigations of the borated water system pipe cracks have shown that cracking is intergranular and occurs in a similar pattern to pipe cracking in BWRs. Obviously the major similarity between BWR pipe cracking and PWR cracking is in the oxidizing environment needed to initiate cracks. The steady-state BWR environment consists of high-purity water at 288 °C containing dissolved oxygen while the PWR cracks have been observed at lower temperatures with concentrated boric acid in connection with air leakage.

Thiosulphate and tetrathionate anions lead to cracking of sensitized AISI 304 stainless steel and the potential range over which IGSCC occurs corresponds to a region for the metastable sulphur oxyanions in which thiosulphate and tetrathionate are capable of being reduced to elemental sulphur. A strong synergistic effect exists between thiosulphate and chloride. When mixed together the thiosulphate and chloride produced more pronounced IGSCC than either thiosulphate or chloride separately. This problem was solved by maintaining high-purity water chemistry and using AISI 304L steel to prevent sensitization.

Irradiation assisted stress corrosion cracking (IASCC) is a time-dependent phenomenon, which needs a minimum residence time or threshold fast neutron fluency to occur, Fig. 8. IASCC can occur at very low stresses, but there is an apparent fluency threshold $>5\times10^{20}$ n cm^{-2} (E > 1 MeV) as perceived today. In addition to the microstructural changes caused by the radiation segregation, radiation hardening, irradiation creep and increase in the oxidizing power of the environment contribute to IASCC. In the case of cracking incidents, like cracking observed in the core shroud welds of BWR's, only some of these effects caused by the irradiation may have been involved.

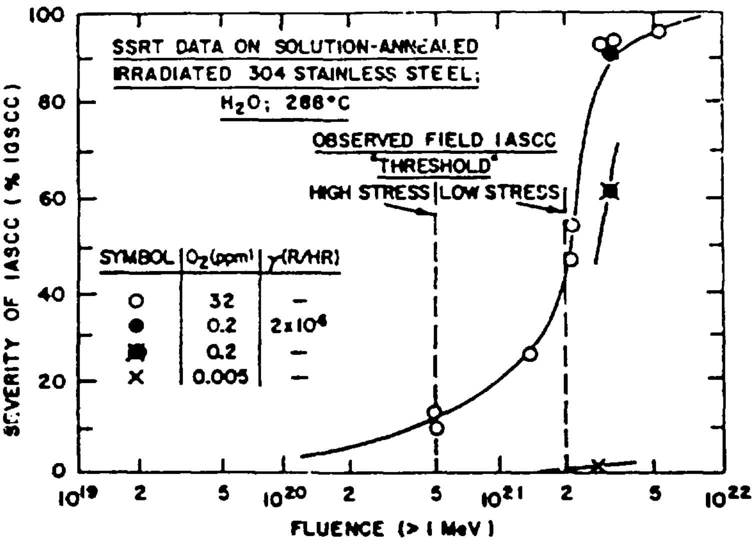

Fig. 8. Relationship between the severity of intergranular stress corrosion cracking and fluency for irradiated type 304 stainless steel under slow strain rate conditions in water at 288°C containing different amounts of oxygen (Andresen, 1989).

5 CONCLUDING REMARKS

Of various types of corrosion problems in the nuclear industry, stress corrosion and corrosion fatigue have been the most important causes of failures in reactor pressure boundary materials. These environment sensitive cracking incidents in pressure vessels, piping and heat exchanger have given rise to safety concerns and have led to the replacements of some major components after only a small fraction of their design lifetime. Improvements in the material technology may not help any more the existing power plants with their problems. However, improvements in the field of water chemistry control, more stringent guidelines and improvements in the on-line monitoring technology due to new high temperature sensors have excellent changes to prevent cracking incidents in the future.

Many of the above failure modes are time-dependent and, thus, are expected to become more prevalent with ageing power plants. For safe operation in the future various ageing assessment techniques, such as NDE, statistical methods, transient data collection, water chemistry control and operational strategies and predictive models for various forms of failures have to be developed.

6 REFERENCES

Aaltonen et al. 1992. Shutdown water chemistry and dissolution of activated corrosion products at Loviisa 1 PWR. In: Tunturi, P. J. (ed.). Proc. of the 12th Scandinavian Corrosion Congress & Eurocorr '92. Vol. 2. Espoo, Fincorr. Pp. 77-88.

Andresen, 1989. In: State of Knowledge of Radiation Effects on Environmental Cracking in Light Water Reactor Core Materials. Cubicciotti, D. (ed.) Proc. of the fourth international symposium on environmental degradation of materials in nuclear power systems - water reactors. Jekyll Island, Georgia, 6 - 10 August 1989. Palo Alto, CA: Electric Power Research Institute, pp. 83-121.

Berry, W. E. 1984. Corrosion problems in light water nuclear reactors. Materials Performance, Vol. 23, No. 6, pp. 9-23.

Bignold, G. J., Garbett, K., Garnsey, R. & Woolsey, I. S. 1980. Erosion-corrosion in nuclear steam generators. Proc. 2nd meeting on water chemistry of nuclear reactors. London: British Nuclear Engineering Society, pp. 5-18.

Cullen, W. H. (ed.). 1986. Proc. 2nd IAEA Specialists' meeting on subcritical crack growth. Sendai, Japan 1985. NUREG/CP-0067 MEA-2090, Vol. 1. 485 p.

Cullen, W. H. (ed.). 1986. Proc. 2nd IAEA Specialists' meeting on subcritical crack growth. Sendai, Japan 1985. NUREG/CP-0067 MEA-2090, Vol. 2. 513 p.

Dörr, A., Odar, S. & Schub, P. 1986. Stages of development of secondary water chemistry in pressurized water reactors. VGB Kraftwerkstechnik 66, 11, pp. 921-933.

Gilman, J. D. 1986. Application of a model for predicting corrosion-assisted fatigue crack growth in LWR environments. Proc. 2nd IAEA Specialists' meeting on subcritical crack growth. Sendai, Japan 1985. NUREG/CP-0067 MEA-2090, Vol. 2. pp. 365-84.

Heitmann, H. G. & Schub, P. 1983. Initial experience gained with a high pH value in the secondary system of PWRs. Proc. 3rd meeting on water chemistry of nuclear reactors. London: British Nuclear Engineering Society. pp. 243-252.

EPRI NP-4946-SR. 1988. BWR Normal Water Chemistry Guidelines: 1986 Revision. Palo Alto, CA: Electric Power Research Institute, September.

EPRI NP-7077. 1990. PWR Primary Water Chemistry Guidelines: Revision 2. Palo Alto, CA: Electric Power Research Institute, November.

EPRI TR-100265. 1992. Radiation-Field Control Manual. 1991 Revision. Palo Alto, CA: Electric Power Research Institute, March.

Hänninen, H. & Aho-Mantila, I. 1985. Environment sensitive cracking in light water reactor pressure boundary materials. Eurotest Conference: Remanent Life: Assessment and Extension. Brussels, 19 - 21 March 1985. 23 p.

Hänninen, H. & Aho-Mantila, I. 1986. Umgebungsinduzierte Rissbildung bei Werkstoffen in druckfürenden Bauteilen von Leichtwasserreaktoren. Der Maschinenschaden, Vol. 59, No. 4, pp. 154-65.

Hänninen, H., Aho-Mantila, I. & Törrönen, K. 1987. Environment sensitive cracking in pressure boundary materials of light water reactors. International Journal of Pressure Vessels and Piping, Vol. 30, No. 4, pp. 253-291.

Kekkonen, T., Aaltonen, P. & Hänninen, H. 1985. Metallurgical effects on the corrosion resistance of a low temperature sensitized welded AISI 304 stainless steel. Corrosion Science, Vol. 25, No. 8/9, pp. 821-36.

Norring, K. & Rosborg, B. 1984. A compilation of experience of corrosion in Nordic nuclear power stations. Studsvik, Sweden, Report EI-84/150. 24 p. + app.

Rieß, R. 1993. Control of water chemistry in operating reactors. IAEA Meeting on influence of water chemistry on fuel cladding behaviour. Rez, Czech Republic, October 4 - 8, 1993.

Scott, P. M. 1985. A review of environment sensitive fracture in water reactor materials. Corrosion Science, Vol. 25, No. 8/9, pp. 583-606.

Stahlkopf, K. E. 1982. Light water reactor pressure boundary components: a critical review of problems. In: Steele, L. E., Stahlkopf, K. E. & Larsson, L. H. (eds.) Structural integrity of light water reactor components. London: Applied Science Publishers, pp. 29 - 54.

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ANALYSIS OF CORROSION DAMAGES OF NPP EQUIPMENT AND CORROSION-MECHANICAL STRENGTH OF RPV MATERIALS

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ABSTRACT

The report discusses the most typical corrosion damages, which took place at NPPs with VVER-440, VVER-1000, RBMK-1000 and RBMK-1500 reactors during their operation period up to 20 years. And in this case the damages both in reactors without cladding (VVER-440) and in reactors, the inner surface of which is protected with the austenitic cladding, are considered.Besides pressure vessels, the analysis is given of typical cases of the corrosion and erosion damages in steam generator elements, made from pearlitic and austenitic steels, in piping weldments of the primary circuit and in dissimilar welded joints. Basing on the review of cases of local corrosion failures, the problems of general corrosion of NPP equipment elements, corrosion-fatigue strength on the crack initiation and propagation criterion, corrosion cracking at static loading of steels and welded joints are considered. A high corrosion and mechanical strength of materials in the process of NPP operation is shown, when there are no preconditions, leading to the break of water-chemical regime of water environment both for VVER type reactors and reactors of RBMK type.

The report is presented at the Specialists Meeting on Erosion and Corrosion of Nuclear Power Plant Materials, Kiev, Ukraine, 19-23 September 1994

INTRODUCTION

Central Research Institute of Structural Materials «Prometey» is the largest material science organization of our country in the field of nuclear power. The Institute activities encompass the development of base and welding materials, which would permit to provide the necessary level of properties and characteristics, responsible for fracture process, as well as their stability under the influence of operation factors. One of these factors is coolant effect on material. Due to the statistic data from 31 to 41% of the total number of the damages of NPP pressure vessels and pipings during operation is associated with the nucleation of pittings, pits, corrosion-fatigue cracks and other defects of corrosion type. The main task of this report is:

- to show, that the problem of NPP equipment corrosion and mechanical strength is an urgent problem and consequently to pay attention to the most typical cases of the primary circuit element damage;
- to present the main investigation results on corrosion and mechanical strength of materials, used for the production of the primary and secondary circuit of NPP with VVER-440 and VVER-1000.

1. MAIN TYPES OF THE EQUIPMENT CORROSION DAMAGE

In a long period of operation (for more, than 25 years) of NPP equipment with water-water coolant, damages of corrosion type took place both in pressure vessels and collectors and pipings of the primary circuit, as well as in heat exchanging tubes. It is known, that pressure vessels of VVER-440 reactors (modification 230) were partially fabricated without anticorrosive cladding. A great number of corrosion damages of pitting type was typical of them. The first line of such reactors is the third block of Novo-Voronezh NPP, the operation of which began since 1971. Fig. 1 shows the density of distribution of corrosion damages, expressed by the number of pittings on 1 m^2 of inner surface. As it is seen from the presented results, the maximum density of pittings is observed in three zones: flange joint, shell of core zone, and reactor pressure vessel bottom. The causes of such density in these zones are different and associated. Density in these zones are different and associated with slime accumulation and irradiation. Such considerable corrosion damage of the pressure vessel inner surface made it necessary in future provide the protection of this surface with anticorrosive cladding and it was assumed as a basis by the fabrication of VVER-440 and VVER-1000 reactor pressure vessels [1, 2].

At the operation of VVER-440 reactor pressure vessels corrosion and mechanical damages were also observed in the region of

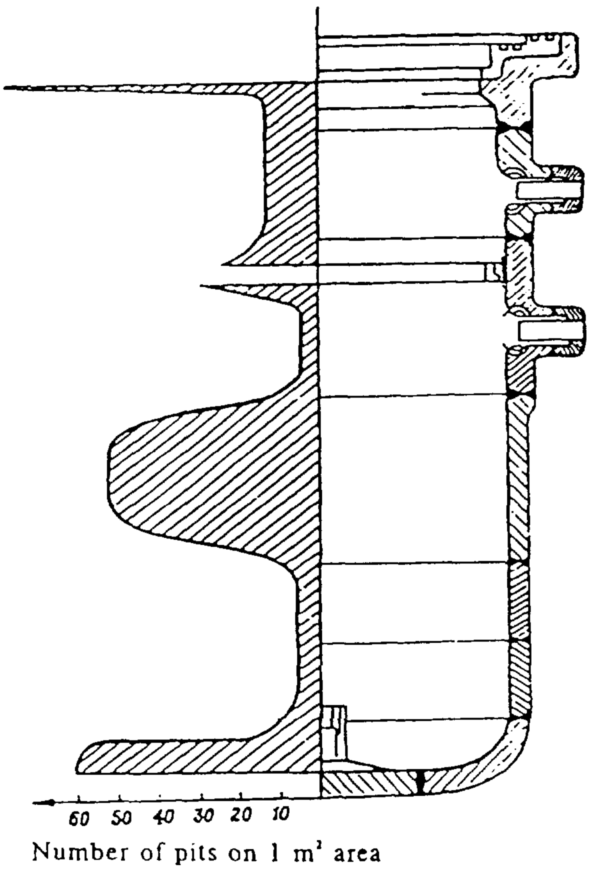


Fig.1 ‘Distribution density of corrosion damages for various pressure vessel zones of the third block of Novo-Voronezh NPP.

the dissimilar joint of the nozzle area, made from pearlitic steel, with the piping of the primary circuit, made from austenitic steel. At the same time it should be noted, that after more, than 25 year operation period, the depth of corrosion and mechanical damages was equal to 3-5 mm, though on one welded joint on the fusion line of forced austenitic cladding and 15X2MFA reactor steel the crack depth exceeded 11 mm, and its extent on circumference was equal to half-perimeter.

One of the typical NPP equipment in-service damage was stress corrosion cracking of collectors at the attack of the primary circuit coolant. As for the production of PGV-440 and PGV-1000 different structural materials were applied (corrosion resistant austenitic 08X18H10T steel for a steam generator of lower power and pearlitic 10ГH2MFA steel for the second type), the nature of corrosion damage is not identical. Thus, for PGV-440 steam generator collectors there are four zones of possible local increase of coolant aggressiveness : zone of variable wetting, where chlorides accumulation is possible; the bottom part of a collector, where slag accumulation takes place; zone of cover and pressure vessel joining and in the region of joining a heat transferming tube with a collector wall. A great number of crack-type damages has a typical transcrystalline character.

During operation of NPP with VVER-1000 reactors steam generator collectors damage also took place. The damages on all collectors were cracks, located in the vicinity of the boundary of perforated and unperforated parts of collectors on seanting cross-pieces between holes in the region of collector undrilled wedge-shaped part, as well as in the area of passing of one vertical set of holes over the wedge-shaped part. Such cracks were in most cases revealed on out let «cold» collectors. The investigations of metal in the vicinity of failure zone showed, that the cracks were successively failed cross-pieces between neighbouring heat exchaging tubes and are of corrosion and mechanical generation. The beginning of cracks generation occurred on the mechanism ofingranular fracture,which then turns into transcrystalline and mixed cracking under the effect of high stresses (total, residual, production and operation) and corrosive environment, especially active in crevice clearance. Such clearance with the size 0.2 mm was the results of the lack of tube expansion in the hole at the distance up to 20 mm from the surface of the second circuit.

The information analysis of steam generator heat exchanging tubes reliability showed that the main cause of their removal appears to corrosion cracking. This type of damage was observed, as a rule, from the side of the secondary circuit, the coolant of which either contained an increased quantity of chlorides and alkali,or may enrich itself with them due to evaporation at the hot heat-removing surface in crevices and clearances on the boundary steam-water.

Thus, the operation experience of NPP equipment shows, that corrosion and mechanical damages may appear in various structure components. Various materials, namely, steels of different structural class (pearlitic and austenitic), welded joints and welds, metal of anticorrosive and buttering cladding are subjected to such kind of damage. And such damages may occur both in the initial period of operation, and later. The expert study of the reasons of corrosion and mechanical damages demonstrates that fracture mechanisms may be quite different.

Therefore, it becomes necessary to take into account the corrosion situation in local zones in structure elements, designed in accordance with the normative documentationand thus to obtain experimental results on the influence of water environment on fracture characteristics, which are responsible for this process. The next section of this report considers these data for materials and their welded joints, widely used for the production of pressure vessels, steam generators and pipings of the primary and secondary circuit of the nuclear power plants VVER-440 and VVER-1000.

2. MAIN INVESTIGATION RESULTS

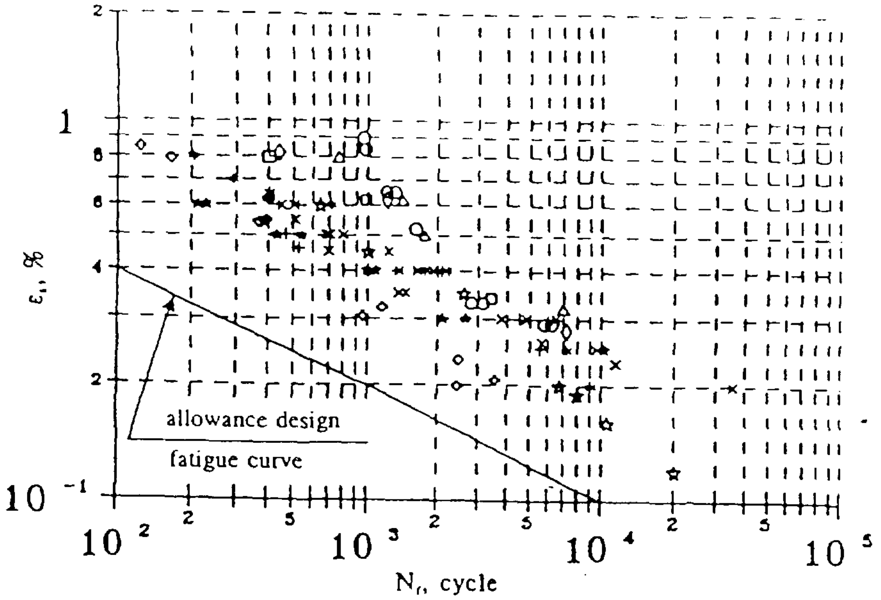
Before considering the investigation results of corrosion and mechanical strength of reactor materials it is necessary to discuss the problem of general corrosion of 15X2MFA steel. This problem became especially important in connection with the operation of pressure vessels without anticorrosive cladding, which were manufactured from this steel. In these investigations it was studied both general corrosion and crevice and contact corrosion of base and weld metal, manufactured by submerged arc welding with Cb-10XMFT wire and AH-42 flux under the influence of primary circuit coolant [3, 4]. It was found, that boric acid presence in reactor water increased only corrosion of pearlitic steel in operation period. Thus,the obtained results showed,that the reactor steel and its weld could be considered to be corrosion resistant materials.

Now, consider the environment LWR effect on the reactor material behaviour from the mechanistic point of view. The fracture process is known to take place in 3 phases: nucleation, propagation and instable crack growth. Hithero, in russian documentation [5] to base NPP equipment service life one takes into account only two stages; crack initiation under the influence of cyclic loadings and brittle fracture as a result of its instable growth. At the estimation of NPP component cyclic strength the stage of crack incremament is not taken into consideration in russian Norms, though in reality by revealing defects this stage of failure has a decisive importance. At the same time in the American Code ASME Section XI [6] there are crack growth curves, which permit also to take into account crack increament in the process of operation. It is already known, that coolant can influence on each failure stage and this influence may be difference at each stage. Therefore, the further discussion of the results of fracture resistance under the coolant influence will be performed for each stage separately. But before the consideration of experimental results it should be noted, that in the world there are no standards yet for the conduction of tests in water environment at high temperatures and pressures. There are exact requirements both to the equipment for such tests and to the parameters and water composition. To our opinion, it is one of the causes of a large scatter of experimental data, and it becomes difficult to compare and interpretate them.

2.1. LOW CYCLE FATIGUE

The investigation results abroad show, that the main parameters, which effect on low cycle fatigue resistance of low carbon and low alloy steels in LWR environments are believed to be: level of the dissolved oxygen, temperature, sulfer content, strain rate and wave shape of the loading. It is established, that the environmental effects on fatigue life at very low content of dissolved oxygen are absent. In oxygenated environments fatigue life depends strongly on strain rate and temperature. At present, basing on the obtained results and revealed laws of the influence of LWR environment on low cycle fatigue of carbon, low alloy and austenitic stainless steels, western specialists offer the new current design fatigue curve of ASME Code Section III.

In Russia systematic low cycle fatigue investigations of reactor materials under the influence of LWR environments were not performed. It is assumed, that the introduction of margins n_s= 2 on the relative elastic stresses and n_N= 10 on the number of cycles to crack generation (at standardized calculation of cyclic strength) should overlap the coolant effect. The available in our time data on low cycle fatigue in water environment for steels, applied for NPP equipment production, are mainly obtained at the solution of some concrete problems, connected with VVER operation. Fig.2 gives low cycle fatigue test results of specimens, carried out in our Institute as well as the results, taken from publications [7, 8]. Inspite of the difference in test methods and various composition of investigated water environments, the obtained data appear to be a good confirmation of the assumed coefficients of cyclic strength margin. Now consider some available results in details. The first conclusion, drawn from the data in Fig.2 (which agree with the data, obtained for SA-106, SA-508, SA-533 steels) is the absence of the lifetime reduction of 15X2MFA and 10ГH2MFA pearlitic steels, 08X18H10T austenitic steel at low cycle loading in reactor water, which does not practically contain oxygen (< 0.01 mg/kg). The environment chemical composition is different for



	Steel	Specimen	Equipment	Test conditions		Water environment
				T, °C	f, Hz	
☆	low carbon 20	smooth cylindrical ϕ = 10 mm	static autoclave	300	0,083	pure water
✻	low alloy 15X2MFA	smooth cylindrical ϕ = 10 mm	recirculating loop	290	0,017	water PWR $[O_2]<10$ppb
+		tubular external ϕ = 24 mm	static autoclave	270	0,0085	water PWR $[O_2]<10$ppb
×		t_{wall}=1,6 mm			0,17	
★	15X2NMFA	-"-	-"-	-"-	0,17	-"-
✙	10GN2MFA	smooth cylindrical ϕ = 10mm	recirculating loop	290	0,017	water PWR $[O_2]<10$ppb
●				270	0,067	pH4,3 $[O_2]$=0,5ppm
○			static autoclave	280	0,083	pure water
□						pH4
△				320		pure water
◊						pH4

Fig.2. Results of constant-amplitude strain range tests (R=-1) in high temperature water.

15X2MFA steel and for 10ГH2MFA and 08X18H10T steels. In the first case, it approximates to the primary circuit coolant composition (water of high purity with boric acid additions), and in the second case – to the secondary circuit coolant composition (a definite content of Cl^- and Na^+ concentration was kept). But, as it was mentioned above, in both case the water environment effect was absent. Besides, the testing of 10ГH2MFA steel specimens in water with pH 4.3 did not cause any changes. The extension of exposure in the primary circuit water at the prolonged cyclic deformation up to 820 hour according to [7], does not also influence on 15X2MFA steel low cycle fatigue resistance. The test results of specimens at biaxial stress state and loading frequences, which differ by 20 times (0.0085 and 0.167 Hz) coincide practically with each other and with the data, obtained in argon. The absence of water environment effect on fatigue strength of pressure vessel materials may be explained by the formation of protective magnetitic film on the inner surface of the investigated specimens, the composition of whichg corresponds to Fe_3O_4. The film, being formed by small levels of strain is practically not damaged by cyclic loading. By a sufficiently large strain amplitude a magnetitic film, as a rule, fails. However, it is not practically reflected on material service life. Such effect is explained by a fast healing of film damages in the environment of neutral parameters, therefore pits at the specimen surface have no time to generate. The maintenance of water regime (absence of free access of oxygen to the surface of structure metal, being deformed) is an additional guarantee of the fact, that the corrosive environment will not promote the service life decrease.

2.2. CRACK GROWTH RATE

Now consider the second stage of fracture and in particular environment effect on fatigue crack growth. In the publications [9-13] it was shown, that fatigue crack rate growth in water corrosive environments was determined not only by stress-strain condition, characterized by stress intensity factor, but also by electro-chemical condition at the developing crack tip, which may be described by the index pH and the metal potential. Such equation for the definition of fatigue crack growth in the material, contacting with corrosive medium, for which the conditions at the specimen tested are characterized by the parameters pH_t and j_t, has the form

$da/dN = f(C_i, Kmax, pH_t, j_t)$. There is a direct correlation between fatigue crack growth rate and electro-chemical conditions at the crack tip. It is seen from the fact, that quite certain electrochemical conditions at the crack tip correspond to each value of crack growth rate on the cyclic failure diagram (Fig.3). And at each part of the diagram the regularity of pH_t and j_t parameter variation is its own. Only for specimens of small thickness (up to 4–5 mm) the conditions

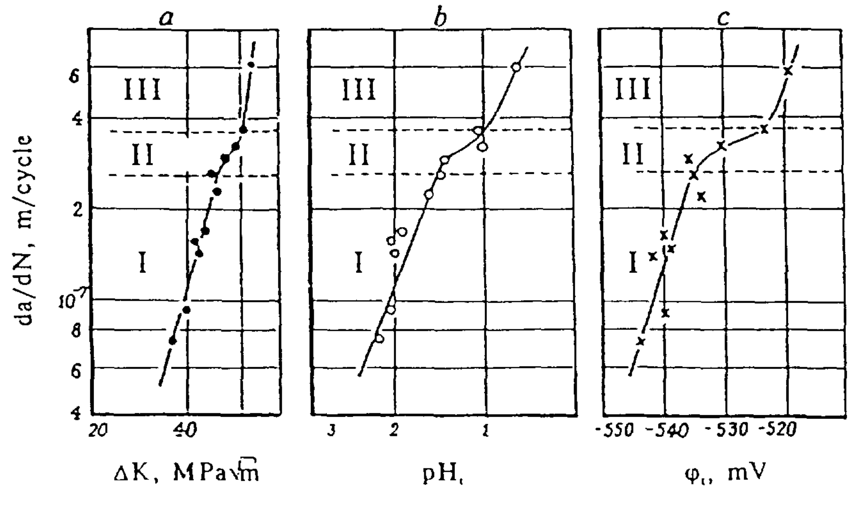


Fig.3. The dependence of fatigue crack growth rate of 15X2MFA steel in water environment at 25°C at pH8 on the range of stress intensity factor (a), hydrogen index of environment pH_t (b) and metal electrode potential φ_t at the crack tip.

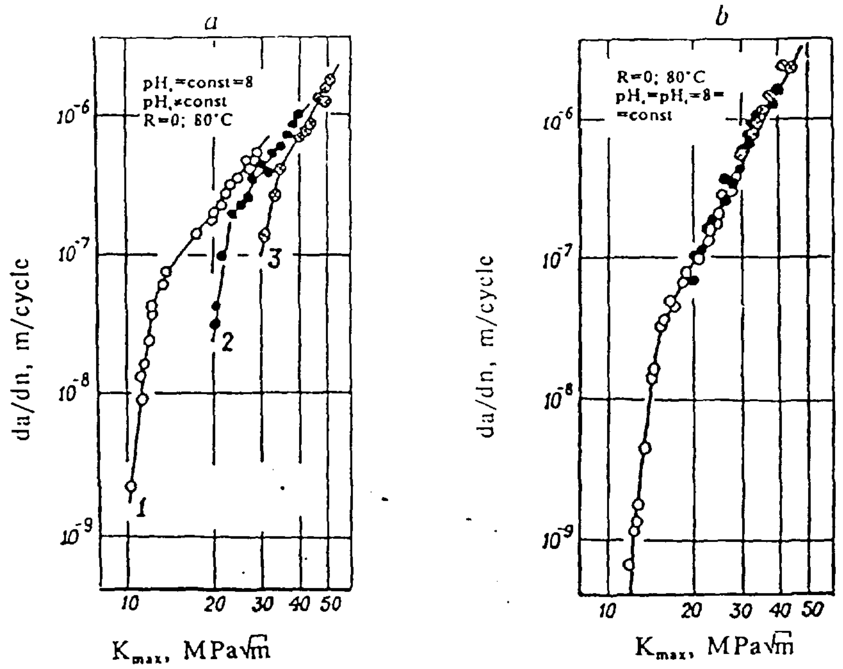


Fig.4. Fatigue crack growth data for 15X2MFA in water at pH8 and 25°C:
a – 1 – ΔKinit=10MPa√m; 2 – DKinit=20MPa√m; 3 – ΔKinit=30MPa√m; pH_s at the surface and pHt at the fatigue crack tip – differrent;
b – pH_s at the surface and pH_t at the fatigue crack tip – equal.

at the surface and at the crack tip are identical, by greater thickness they may differ sufficiently. The construction of invariant diagrams of cyclic material fracture toughness in corrosive environment specifies pH and j_t to be constant. For this purpose the Physical and Mechanical Institute [13] developed the procedures, which permitted to measure the above mentioned values and to provide their constancy at the propagating crack tip. As an example of this approach realization Fig.4 gives the results on crack growth rate in 15X2MFA steel at 80°C in water environment, obtained on the traditional procedure and dependent of the initial conditions of loading, as well as the results, obtained under the similar electrochemical conditions at the crack tip (pH_t= const, j_t= const) in the process of its propagation.

Investigations of the influence of different technological and service factors on fatigue crack growth resistance of pressure vessel materials in air show that crack rate (da/dN) in real value interval of the stress intensity factor DK range is slightly dependent of assymetry loading factor and can be described by Paris one-parametric dependence da/dN = C (DK)^m, where C and m are constants. This result forms the basis of internal crack-like defect increment ASME Code design in reactor materials used in USA Nuclear Engineering [6]. For this purpose for PWR materials used in our country Paris relation dependence withconstants $C = 5.8x10^{11}$ and m = 2.6 was suggested [10]. At the same time at high temperature the aqueous medium fatigue failure process description is too complicated. It was established that in this case fatigue crack growth rate for the type of materials mentioned depends upon such mechanical factors as frequency, asymmetry, loading cycle shape [14, 15], chemical composition of material, degree of non-metallic impurities [16, 17] and on coolant temperature [18]. That's why the standard suggestion development considering stage of crack kinetics in reactor materials under the influence of the coolant should be based on data including all factor combinations mentioned above in order to make it possible to estimate the degree of conservatium for the performed design of surface defects increament for the operation of reactor vessel.

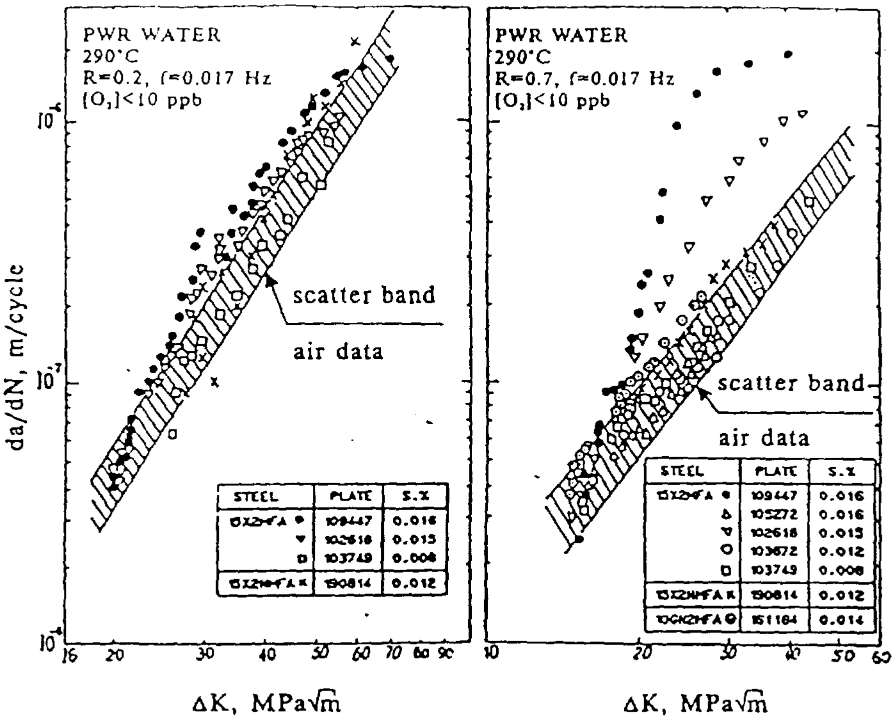


Fig.5. Fatigue crack growth rate in low alloy steels in deoxygenated water environment at 290°C.

Our Institute developed the investigation program of cyclic fracture toughness of reactor materials under the influence of high temperature water environment, simulating the coolant composition of VVER primary circuit, in which 15X2MFA, 15X2HMFA and 10ГH2MFA steels were included, as well as their welded joints, produced by submerged arc welding.

At the beginning of the investigations the kinetic diagrams of fatigue fracture in air at 290°C and two coefficients of loading cycle asymmetry were obtained. Further, they were used for comparison with the similar data, obtained in water environment to estimate quantitatively the environment effect. All tests were carried out on compact specimens of 25 and 50 mm thickness. To investigate the effect of water environment of high parameters both autoclave KT, established on the standard testing machine UME-10T, and the installation of firm Huber, which includes autoclave and circulating circuit with water composition control were used.

It is common practice to obtain the experimental data on structural materials fatigue by applying high-frequency tests within the limits of the reasonable duration of experiment. In practice, power engineering equipment is designed to operate over several decades therefore there is an inevitable disparency between the predicted endurance and the duration of experiment. The gap is of no importance if the service conditions are free from other time dependent processes promoting the failure evaluation. However, these processes take place in corrosive environment [19] and the time factor must be taken into account.

The test results showed, that for all materials (except two heats of 15X2MFA steel) the water environment effect is practically not observed both at R = 0.2 and R = 0.7 (Fig.5). Specimen tests for 5 heats of 15X2MFA steel in air did not reveal difference in crack growth rate, the result located in a narrow scatter band, typical of fatigue. For this steel with < 0.012% S the crack growth rate in water and in air is the same. But for steel with greater S content the influence may be different. Sulphide marks, made from specimens from three 15X2MFA steel heats with practically the same S content (0.015 and 0.016 w.%) in the plane parallel to the crack propagation plane showed the different distribution and morphology of MnS. Thick-plate material (S = 0.016%) is characterized by the presence of large stretched MnS. In forgings with S = 0.016%, manganese sulphides

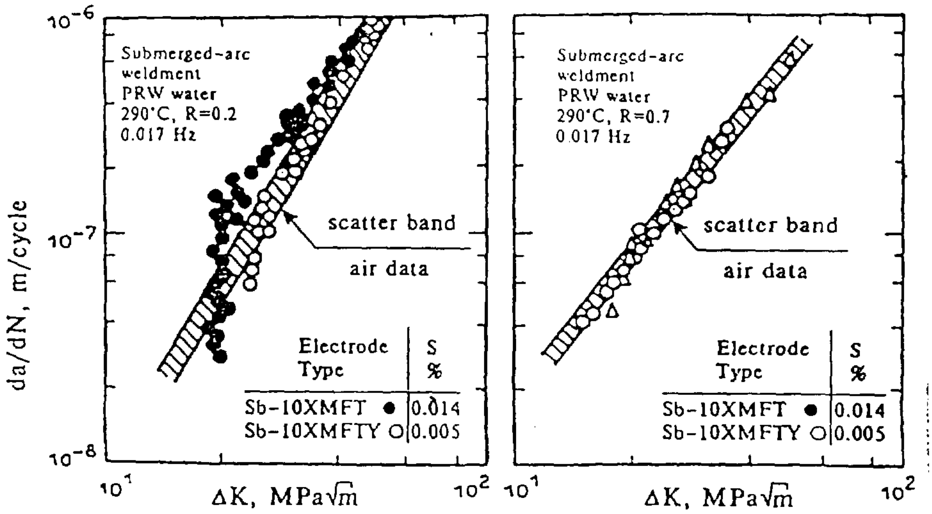


Fig.6. Effect of PWR environment on fatigue crack growth submerged-arc weld metals.

inclusions are fine-dispersed isolated and chaotically scattered globulus, while in forgings with S = 0.015% they locate sufficiently uniformly but have a stretched form and a large size.

Taking into account practically the similar S content one may state, that such great difference of the principle parameters of non-metallic phases is the main reason of crack growth process acceleration in two heats of 15X2MFA steel, which is confirmed well by the results of finnish specialists [20]. The same behaviour is observed for weld metal, produced by submerged arc welding (Fig.6).Thus, due to the application of pure materials at steel melting, it is possible to increase essentially failure resistance at the stage of crack propagation at the coolant attack.

2.3. STRESS CORROSION CRACKING

By considering the influence of high temperature water environment on crack propagation at static loading of reactor materials, it is necessary to note a practically complete absence of data on this problem in russian publications. In our Institute the investigations in this direction were performed for 15X2MFA, 15X2HMFA and 10ГH2MFA steels. For two first steel types, the metal was tested on two strength levels. Thus, it was taken into account, that in the process of operation under the influence of neutron irradiation, the strength characteristics of 15X2MFA and 15X2HMFA steel increased. To simulate such influence one uses heat treatments, consisting of standard quenching with a subsequent low temperature tempering.

The investigations were carried out in special autoclaves, designed to operate at the environment temperatures up to 350°C and pressure 15 MPa, which were installed in AIMA-5-2 testing machine. Compact specimens of 15 and 25 mm thickness with a fatigue crack, obtained at preliminary cyclic loading in air, were tested.

All experiments were carried out in the deoxygenated water environment, but because of the circulating circuit absence, the environment composition was not controlled in the process of testing.The test conditions and the obtained results are given in Table. Irrespective of strength level the investigations of 15X2MFA and 15X2HMFA steel fracture toughness at static loading for 15000 hours did not reveal the tendency of these materials to cracking at the water environment temperatures 250 and 290°C. At less base of testing up to 7000 hours an analogous result was obtained for 10ГH2MFA steel for two compositions of water environments. The experiments in water environment with low pH and high content of chlorides are caused with the fixed at operation devialions in the secondary circuit coolant chemical composition.

CONCLUSION

The presented results clearly demonstrate, that russian pressure vessel heat resistant steels and their welded joints have sufficiently high stress corrosion resistance in water environment of high purity by long-term static and cyclic loading. And to prevent the generation of corrosion damages first of all it is important to provide small oxygen concentration in coolant both by design and transient conditions. Even by the presence of surface damages in anticorrosive cladding, their penetration in base metal (weld) during the whole period of equipment service life will not take place, due to the revealed effect of crack retarding on the fusion line of austenitic cladding and pearlitic material. It permits to guarantee corrosion and mechanical strength of NPP equipment welded joints with water-water coolant, 440 and 1000 MWt power, produced from the heat resistant steels – 15X2MFA and 15X2HMFA.

Table

CONSTANT LOAD TEST RESULTS (STATIC AUTOCLAVE)

Water Chemistry (Start-Up)	Material	Heat	YS MPa	T °C	Speci-men	Code	K_I MPa√m	Exposure hours	Environmetal Cracking
$[O_2]<5$ppb $[Cl^-]<50$ppb B as H_3BO_3 - 8000ppm pH (room temperature) - 8,0	15X2MFA plate	103219	600	250	CT15	CL3	40	1000	no
						CL2	45	7000	no
						CL7	45	12000	no
				270		CL6	45	14000	no
				290		CL8	45	14000	no
			1100	250		CHL1	56	1000	no
						CHL2	58	7000	no
						CHL3	60	12000	no
						CHL4	62	15000	no
	15X2MFA forging		580	290	CT25	KT1	52	7000	no
						KT2	56	12000	no
	15X2HMFA plate	135340	630	250	CT15	BKB1	40	1000	no
						BKB4	45	7000	no
						BKB6	45	12000	no
			990	250		BKB3	55	1000	no
						BKB10	57	7000	no
						BKB11	55	12000	no
				290		BKB2	58	12000	no
						BKB5	60	15000	no
$[O_2]<5$ppb $[Cl^-]<50$ppb pH (room temperature) - 7,8	10GH2MFA forging	161181	570	270	CT15	MBC1	35	2500	no
						MBC2	40	4000	no
$[O_2]<5$ppb $[Cl^-]<3,4$ppm pH (room temperature) - 4,3						MBC8	35	2000	no
						MBC6	40	7000	no
						MBC5	45	2500	no
$[O_2]<5$ppb $[Cl^-]<3,4$ppm pH (room temperature) - 4,3	10GH2MFA forging	11699	500	270	CT15	P4	40	1000	no
						P1	45	1000	no
$[O_2]<5$ppb $[Cl^-]<50$ppb	10GH2MFA forging	112793	560	270	CT25	10-4	55	7000	no

REFERENCES

1. Materials Science Problems by Production and Operation of NPP Facilities. Materials of the First International Science and Practical Conference. 17-21 June 1991. Leningrad. CRISM»Prometey», 280p.

2. Materials Science Problems by Production and Operation of NPP Facilities. Transactions of the Second International Conference 14-21 June 1992. St.Petersburg. CRISM»Prometey», 310p.

3. Alekseenko N.N., Razov I.A., Usatov E.P. Steel corrosion in water with increased content of chlorides under irradiation conditions. Zashchita metallov, vol.XIII, issue 2, 1977, p.185-188.

4. Timofeev B.T. Corrosion and Mechanical Strength of Weldments of NPP equipment. Leningrad, LDNTP, 1985, 26p.

5. PNAE G-7-002-86. Strength calculation Norms for nuclear power plant equipment and pipings. Moscow, Energoatomizdat, 1989, 528p.

6. ASME Boiler and Pressure Vessel Code. Section XI. New York, 1980.

7. Karzov G.P., Litvin V.V., Timofeev B.T., Timofeeva A.I. Effect of different technological and operational factors on resistance to fatigue failure of steel quality 15X2MFA. Voprosy Sudostroenija, Ser.Metallovedenja, 1979, issue 28, p.3-11.

8. Giginyak F.F., Zvezdin Yu.I., Lebedev A.A., Timofeev B.T., Fedorova V.A. Corrosive and mechanical strength of welded joints in steels at elevated temperatures. International Journal on Pressure Vessel and Piping, vol.33, 1988, nr.5, p.359-372.

9. Fedorova V.A., Karzov G.P., Timofeev B.T., Lanetz V.P. Effect of PWR environment on the fatigue crack growth rate of LWR vessel materials. Proceedings of the Third International Atomic Energy Agency Specialists' Meeting on Subcritical Crack Growth. 14-17 May 1990, p.279-288.

10. Timofeev B.T., Fedorova V.A., Zvezdin Yu.I. et al. Resistance of pressure vessel steels and their welded joints to corrosion fatigue fracture at elevated temperatures. Problemy Prochnosti, nr.1, 1987, p.25-31.

11. Panasjuk V.V., Ratych L.V., Zvezdin Yu.I. et al. Cyclic Corrosion crack growth resistance curves for some pressure vessel steels. Fiziko-Khimicheskaja Mekhanika Materialov, nr.3, 1985, p.37-45.

12. Zvezdin Yu.I., Fedorova V.A., Timofeev B.T. et al. Resistance to corrosion fatigue damage in steels at elevated temperatures. Energomashinostroenie, nr.3, 1987, p.27-30.

13. Panasjuk V.V., Ratych L.V., Dmytrakh I.N. About the problem of electrochemical condition determination in a propagation crack by the investigation of materials stress corrosion cracking in corrosive environment. Fiziko-Khimicheskaja Mekhanika Materialov nr.3, 1982, p.43-49.

14. Bamford W.H. Application of fatigue crack propagation in corrosive environment data to analyse nuclear reactor pressure vessel integrity. Transaction of ASME, 1979, vol.101, nr.3,p.1-12.

15. Scott P.M., Truswell A.E., Druce S.G. Corrosion fatigue of pressure vessel steels in PWR environments – influence of steel sulfer content. Corrosion. 1984, vol.40, p.350-357.

16.Van Der Sluys W.A., Emanuelson R.H. Crack propagation in steels for nuclear pressure vessel by testing under the conditions of cyclic loading in light water reactor environment. Transactions of the ASME, 1986, nr.1, p.47-56.

17. Torronen K., Saario T., Wallin K., Forsten J. Evaluation of the effect of metallurgical variables on materials behaviour and reference curves. The International Journal of Pressure Vessels and piping. 1984, vol.15, nr.4, p.251-269.

18. Atkinson J.D., Forrest J.E. Factors influencing the rate of growth of fatigue cracks in PWR steels exposed to a simulated PWR primary water environment. Corrosion Science, 1985, vol.25, nr.8/9, p.607-631.

19. Tice D.R. A review of the U.K. collaborative programme to test the effects of mechanical and environmental variable on environmentally assisted crack growth of PWR pressure vessel steels. Corrosion Science, 1985, vol.25, nr.8/9, p.705-743.

20. Hanninen H., Torronen K., Kemppainen M., Salonen S. On the mechanisms of environment sensitive cyclic crack growth of nuclear reactor pressure vessel steels. Corrosion Science, 1983, vol.23, nr.6, p.663-679.