

INTERNAL CONDENSER TUBE CORROSION ON CONDENSERS AND COOLERS IN POWER STATIONS

by P. H. Effertz, W. Fichte and P. Forchhammer

Presented by :



TAPROGGE Gesellschaft mbH

Schliemannstraße 2-14

58300 Wetter

Germany

Tel.: +49 (0)2335 / 762-0

Fax: +49 (0)2335 / 762-245

E-Mail: info@taprogge.de

Homepage: <http://www.taprogge.de>

INTERNAL CONDENSER TUBE CORROSION ON CONDENSERS AND COOLERS IN POWER STATIONS

INTRODUCTION

Leakages in heat exchangers, where water with a high salt content is used for cooling, have almost always serious effects on the operation of power stations, but the immediate damage bears no relation to the possible consequential damage. In extreme cases, unspotted intrusion of cooling water leads to power breakdowns, e.g. due to tube bursts in the evaporation lines or to turbine blade breakage in the area of incipient steam humidity in the turbine. As a rule, a falling-off in capacity and a prolonged search for the leakage are necessary.

Of the damage to condensers and coolers investigated over the last five years, the major part (> 90%) was due, exclusively or substantially, to corrosion of tubing in the cooling water circuit. Our own experience with damage is restricted to systems in the Federal Republic of Germany cooled with brackish water or river water, and where preference is given to copper alloy tubing. The damage was caused by local corrosive attack on the tubing (1 to 8), whereby a reduction in the frequency of pitting, stress corrosion cracking, erosive corrosion, dealloying and corrosion fatigue was observed.

The high resistance to corrosion of the copper-base tube materials in cooling water is said to be due to the formation of a natural covering film of Cu_2O with a maximum thickness of several microns. This film contains alloy elements in a trace concentration (protective film passivity).

In order to understand the selective corrosive processes leading to damage, it is necessary to examine more closely the initial processes underlying the formation of uniform covering films and their susceptibility to influence.

UNIFORM CORROSION

The oxide films on copper alloys are twofold. They consist of one layer growing from the original surface into the

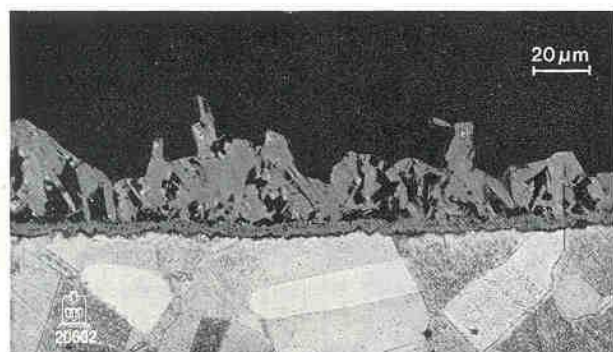
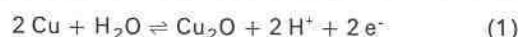


Figure 1. Double-lamellar covering layer $\text{Cu}_2\text{O}/\text{Cu}_2\text{O}-\text{CuO}$ on a heat exchanger tube of CuZn28Sn .

alloy and, secondly, a growing layer with varying conditions of thickness (9, 10). Mostly, the outer layer is formed of loosely linked single crystals only (Figs. 1 and 2).

The topotactic conversion under direct anodic oxidation to Cu_2O , being the anodic reaction at the interface of the phases $\text{Cu}_2\text{O}/\text{Cu}$ -alloy (anode spot), is termed as



Also, a part of the anodic current is taken over by the dissolving reaction of the copper



respectively, its alloy elements (Zn, Ni etc), for example:



The relationship between formation of Cu_2O (1) and the appearance of Cu^+ and Zn^{2+} (2a and 2b) depends on the alloy, since the volume of the corroded alloy film is filled up with the topotactically generated and mainly pure Cu_2O .

Topotactic reactions of the kind described are only possible in the long run if the oxidizing species (H_2O or OH^- ions) can reach the momentary phase boundary and diffuse the ionic reaction products (Cu^+ , Zn^{2+} , H^+). Basically, two transport mechanisms are conceivable: solid diffusion of O^{2-} and Cu^+ ions in the Cu_2O layers (grain or grain boundary diffusion), or ingress and elimination of the oxidizing resp. generated ions via pore channels in the Cu_2O layers through liquid diffusion. In view of the low temperature-conditioned rate of ion diffusion in the Cu_2O lattice, pore diffusion will be the principal transport mechanism. There is metallographic evidence of micro-

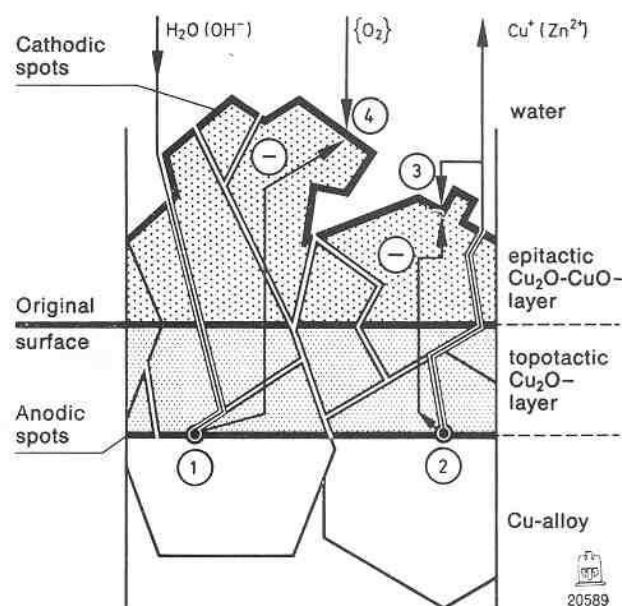
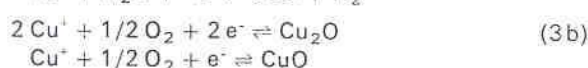
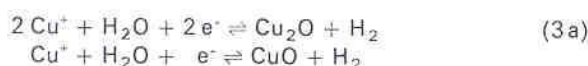


Figure 2. Formation of a Cu-alloy covering layer in water (schematic).

pores in the topotactic Cu_2O layer. The ions produced by the anodic dissolving reaction (2a and 2b) reach the outer surface of the topotactic layer via the pore channels. The one part of these ions is drawn away by the water current, while for the other part there is the possibility of cathodic segregation, with epitactic growth into the top surface of the topotactically grown Cu_2O layer, in accordance with the gross reactions:



In this way, the outer $\text{Cu}_2\text{O}/\text{CuO}$ layer is formed. The same thing occurs, basically, in the case of the emerging alloy ions (Zn, Ni, Fe, Al) whose oxides can thus be integrated, in a minor quantity, into the epitactic Cu_2O layer. Tin remains in the topotactic layer.

The phase interface epitactic $\text{Cu}_2\text{O}/\text{water}$ can thus be regarded as a cathodic spot. Apart from the reactions (3), the reduction of the oxygen dissolved in the water will ensue as the principal cathode reaction, compensating out the anodic reactions



The flow of electrons from the anodic to the cathodic spot occurs in the electron-conducting Cu_2O layers. The anodic and cathodic reactions occurring simultaneously on both sides of the double oxide layer are short-circuited to a corrosion element via electrolyte-soaked and electron-conducting Cu_2O layers. The short-circuit currents which are, in the ideal case, quantitatively alike, and which flow in the numerous, neighbouring microcorrosion elements, determine, with relation to the total macroscopic surface, the momentary rate of corrosion in the alloy with a fully uniform oxidation depth.

The short-circuit current densities and, therewith also, the rates of oxidation are influenced by the difference between the cathode and anode potentials, by the diffusion of the reaction participants in the water to and from the cathodic spots and, finally, by the inner electronic and ionic resistance of the corrosion elements.

In the uniform corrosion of high-Cu alloys in aerated water, the anodic reaction of the Cu_2O formation (1) and the cathodic reaction of the oxygen reduction (4) can be regarded as being potential-determinant. The no-load tension ($\Delta E = 0.757 - 0.0147 \log P_{\text{O}_2}$) of such a cell $\text{Cu}/\text{Cu}_2\text{O}/\text{H}_2\text{O}$, H^+/O_2 (Cu_2O) is formally determined solely by the oxygen concentration in the cooling water. As, in the cooling water, the concentration can only fluctuate within a certain range, its influence on the no-load tension is insignificant (maximum 0.147 mV). Because of the spatial separation of the cathodic and anodic spots, an additional opposite pH value influence on the no-load tension, which is cancelled out in the overall reaction, (1 and 4), can be identified.

Rate-determining significance for the growth of the covering film is imputed to the diffusion of the oxygen dissolved in the water by virtue of the adhering liquid boundary

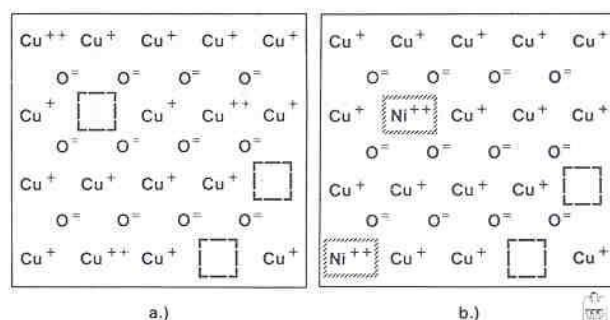


Figure 3. Schematic plan of the defective lattice
a) pure Cu_2O b) $\text{Cu}_2\text{O-NiO}$

layer, at least in the initial stage. In the flooded tube, the process can be controlled only within narrow limits. The inner resistance of the corrosion elements can be substantially influenced by change in the flaw structure of the Cu_2O layers. Cu^+ ions are missing in the lattice of the flaw electron conductor (Fig. 3a). Electron neutrality is produced by additional, positive charges in the neighbourhood of the cation vacancies, whereby the said charges can be regarded as being associated with a neighbouring cation. The high concentration of the defect electrons is the cause of the good electronic conductivity of Cu_2O . If cations of a higher valency are introduced into this vacancy structure or in the place of Cu^+ ions (for example: Zn, Ni, Fe, Sn), there will follow in each case the consumption of one or more defect electrons and, thus also, an increase in the specific electronic resistance of the oxide layer (Fig. 3b). Given an equal difference of electrode potential, the consequence is a diminution of the corrosion current resp. rate of corrosion. This explains the considerable decrease in the rate of corrosion when alloying Ni and Fe into Cu-Ni alloys resp. Zn, Sn and Al into special brass as against pure copper. An introduction of higher-valency cations into the covering film can also ensue via the cooling water. The specific electronic resistance of agglomerated Cu_2O layers to CuNi30Fe increases, as compared with the resistance to pure copper of Cu_2O layers that have arisen in NaCl solutions, by the factor 10 [44]. The rate of corrosion is reduced accordingly.

The unfavourable influence of chloride ions on the corrosion rate of Cu alloys is also explained in terms of a modification in the defect structure of the Cu_2O covering films [44]. In this modification, Cl^- ions replace O^{2-} ions in the oxide lattice. The electron neutrality is attained at each substitution by the transition of a Cu^+ ion into the aqueous medium. It is only now that the neutral cation vacancies additionally formed thereby make possible or easier the outward diffusion of Cu^+ ions into the Cu_2O lattice. Electron neutrality can, in addition, be achieved by excess electrons (enhanced electronic conductivity). By accumulations of vacancies and locally preferred introduction of Cl^- ions (CuCl), highly microporous covering films with improved electron conductivity can be produced.

In chlorided waters, corrosion rates that are from ten to twenty times higher are the result.

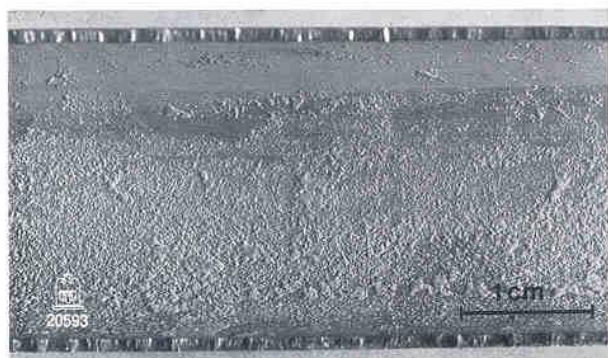


Figure 4. Pin-prick and broad-surface attack under a microporous protective layer of Cu_2O (pickled tube)

It will be clear from these statements that the corrosion rate of copper alloys in cooling water can be effectively influenced by the covering film structure. The model conceptions used for this are based on observations and on partially sifted, theoretical, individual conceptions.

PITTING CORROSION [11 to 16]

In microporous covering layer structures, the short-circuit currents flowing in the individual surface zones are no longer equal, since the electronic and ionic resistance of the covering layer at the defect spots is reduced in comparison to the surrounding area. Greater short-circuit currents in these places are identical with a greater incidence of attack. Tubes with such covering films show more or less finely scarred surface (Figure 4). Although this corrosion shows the symptoms of pitting (pitting hole diameter equal to pitting hole depth), it can be classed as uniform corrosion on account of the very minor absolute depths and the fairly uniform distribution. Only with a hole depth of 0.1 mm and upwards should one speak of pitting.

Origins of pitting

Other conditions, apart from aggressive cooling water*, are necessary for the appearance of such deep local deteriorations (> 0.1 mm). According to our observations, with new tubes in the initial operational phase, these conditions are mainly operationally determined precipitations of solids, surface anomalies due to manufacturing causes and, after longer periods of operation (for example, $> 10,000$ hrs) isolated local damage due to the peeling-off of covering film or to cooling water concentration at

*) The expression "aggressive cooling water" is subjective. From the corrosion standpoint, one will be on the safe side in adding waters with chloride-conditioned conductivities of > 1000 $\mu\text{S/cm}$ and mainly organic bodies in suspension > 10 mg/kg.



Figure 5. Abundant pitting in an auxiliary cooler tube (CuNi10Fe) at the end of the first few operating months.



Figure 6. Sporadic pitting in a condenser tube (CuZn20Al) after six years of operation.

operational down-times. Accordingly, new tubes often show numerous (Fig. 5) pin-prick corrosion areas during the initial operating phase, whereas only isolated cases of pitting are observed over longer operating periods (Fig. 6).

Operationally occurring solids (for example: slime, calcite) can settle in layers on the tubes concurrently with the formation of microporous covering films. Such layers of more or less high conductivity act as expansive cathodic zones in which small uncovered surface can become anodic spots (Fig. 7). The covering largely inhibits the anodic reactions on the alloy surface by stopping-up the porous channels in the still thin Cu_2O -specific covering films. In contrast to this, the anodic reactions evolve at a greater rate underneath the small surface not covered with solid material because the entire cathodic current of the coating surface is available for the anodic dissolution current at that point (theorem of areas). Incipience of pitting at such points is the consequence.

Further spots for the tendency to form deep pitting holes during the initial operating period with new micropore-layered tubes are oxidic or sulphidic slag bands rising to the surface (Fig. 8) and cracked drawing lubricant residues. At the boundaries of the non-metallic inclusions resp. of the sintered carbon particles (Fig. 9), there appear, in the growing specific covering film, fissures which facilitate a mainly unhindered ingress of cooling water resp. the almost unhindered discharge of corrosion products. In conjunction with the relatively good electronic conductivity of the inclusion, an accelerated attack occurs at these boundaries. These spots largely determine therefore the location of the pitting.

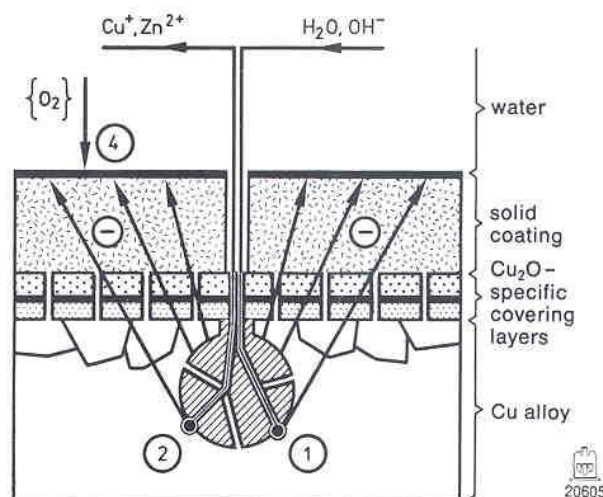


Figure 7. Formation of pitting under extraneous coatings (schematic).

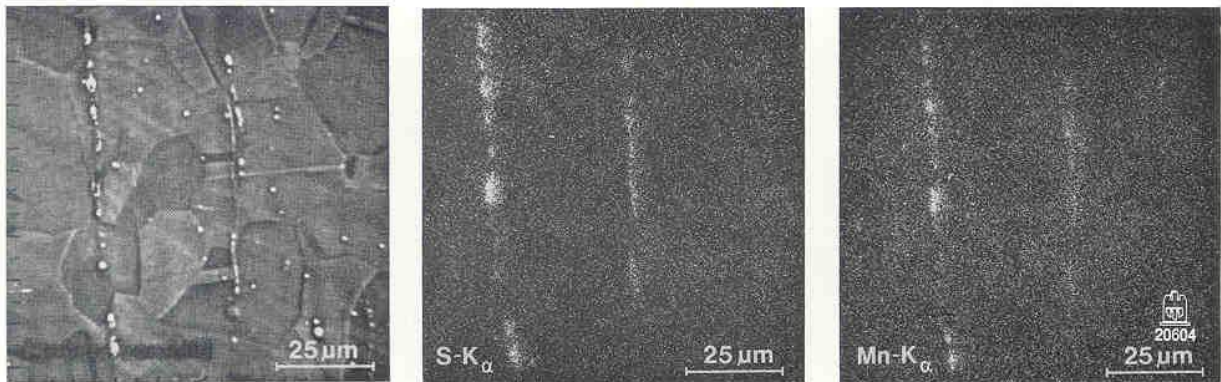


Figure 8. Manganese sulphide slags in CuNi30Fe.

Band structures in heat exchanger tubes resulting from ingot segregations are also said to be places conducive to pitting (Fig. 10).

Early pitting due to operational precipitations and production-borne anomalies on the surface of the material should be countered by the use of continuous cleaning as early as possible and by the employment of new homogenous inclusion-free tubes without traces of residue. A uniform annealing skin is an advantage.

The adhesion and the mechanical stability of natural oxide covering films, which occur in cooling water with a high chloride conductivity, are relatively slight. Dessication during operational down-times can lead to the bursting-off resp. dislodgment of these films. Local exposure of the metallic undersurface in large and mainly undamaged surface areas leads, on resumption of operation, to isolated, anodic spots which become established in large cathodic areas, thus forming breeding zones for pitting.

In drying drops or puddles of cooling water, chemical reactions can bring on the direct destruction of the Cu_2O covering, whereby hydroxides, chlorides, sulphides or carbonates are formed. At such trouble points, the anodic reactions of the alloy element easily become fixed. Points of germination for pitting are here to be found.

Pitting at the end of operational periods, which is caused

by the bursting of covering films and agglomerations, can be widely avoided if, during periods of inactivity, at least a partial flow-through is maintained.

Growth of pitting

The four starting-points of dangerous pitting shown in the sketches are characterized as small-surface anodic spots, surrounded by more or less covering-film-passive surfaces. At these points, there is an accelerated dissolution resp. oxidation of the alloy. The increased Cu concentrations lead via hydrolysis to acidification of the pitting electrolyte. This, in turn, causes a further acceleration of the active corrosion (2 a and 2 b). In contrast to Cu and Sn, the alloy elements Zn, Ni, Fe and Al are, according to the conditions prevailing, and with respect to pH value and potential, only existent in their ionic form and are therefore able to leave the pitting hole in the direction of the cathode (cooling water flow).

By electrolytic transport, anions are reinforced in the pitting hole electrolyte. When the solubility product is exceeded, CuCl , for example, is precipitated as a low-soluble salt.

These conceptions are in keeping with electron diffraction analyses made at pitting locations in special brass CuNi and even in NiCu alloys (Fig. 11).

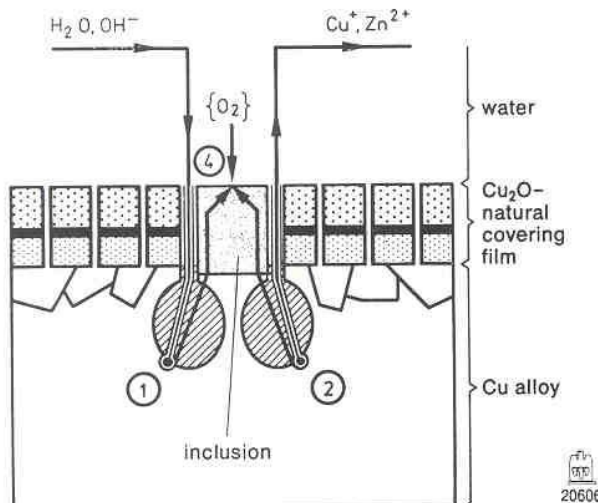


Figure 9. Formation of pitting at an inclusion (schematic).

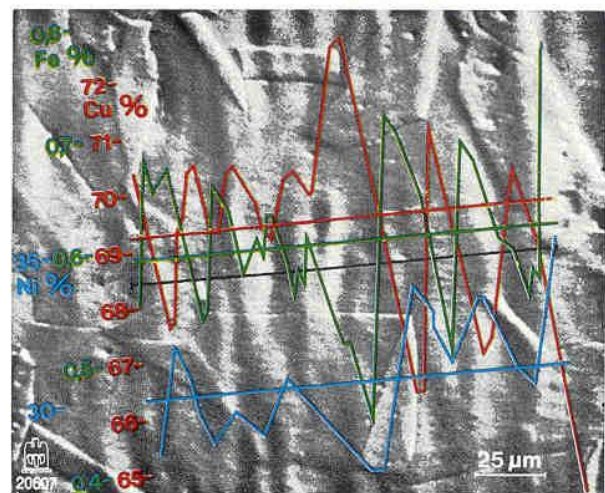


Figure 10. Concentration fluctuations in CuNi30Fe tubes resulting from block segregations.

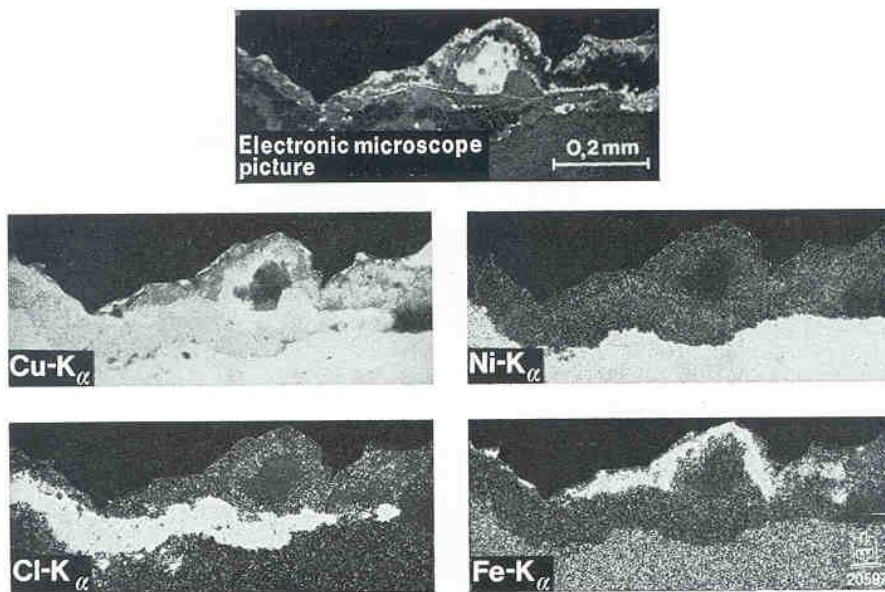


Figure 11. Distribution of elements in a pitting location (NiCu30Fe).

Over longer periods, the pitting depth does not increase in linear relation to the time. Periods of growth and standstill alternate in uncontrolled fashion. Here, diffusion inhibition and change in the covering film geometry exert a powerful influence. With such discontinuous processes, any forecasts as to when the hole will break through are impossible.

There is only a small likelihood of being able to halt the active pitting in the growth stage at all points in the tubing, for example, by applying induced covering films and continuous cleaning. For this reason, decisive countermeasures for preventing the initial formation of pitting should be adopted.

STRESS CORROSION CRACKING [17 to 21]

Stress corrosion cracking in heat exchanger tubes can only be observed in brass alloys. Whereas in former years intercrystalline, longitudinal cracks often occurred in the first operational phases, this being caused by residual stresses from manufacture, such defects have in fact been no longer observed since the introduction of final stress-relief annealing and the adoption of the ammonia test in

acceptance testing. On the other hand — if one disregards the stress cracking resulting from mechanical defects formed on assembly and in operation — there appear nowadays, after longer spells of operation, crosswise transcrystalline cracks, approx. 3 to 5 mm from rolled-in tube ends, which present a serious problem in connection with heat exchanger leakages (Figs. 12 and 13). These cracks in the transition zone are perpendicular to the tensile stresses formed in the tube rolling-in process. Rarely can such damage be attributed to improper tube and tube sheet widenings during the expanding process. It is also difficult, in most cases, to trace the medium NH_3 , noted for its tendency to promote stress cracking, via the continually present concentrations in the cooling water ($< 1 \text{ ppm NH}_3$) or in the coating, ($< 1 \text{ weight } \% \text{ NH}_3$). As raster electron microscope studies of the relevant surface area show, it is significant that such fissures have their origin at points of finest covering film damage in the transition zone.

Now, bearing in mind the theory of stress corrosion cracking, for whose appearance the electro-chemistry of the corrosion processes, the atomistic processes in the deformation at the crack nucleus, and the stress conditions in the component are mainly significant, cracks can be

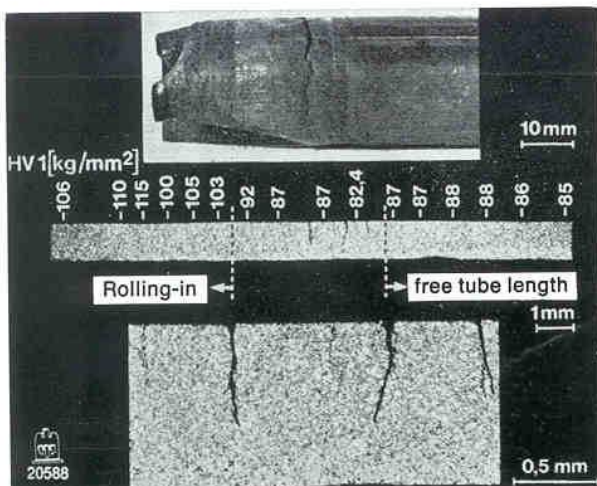


Figure 12. Stress corrosion cracking in the transition between the rolling-in zone and the free tube length.

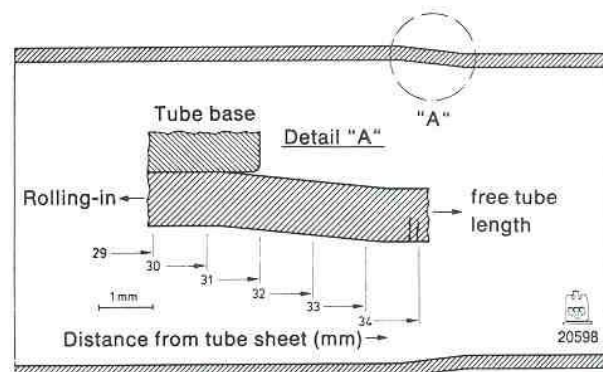


Figure 13. Beading transition (schematic).

explained in terms of the mechanism of stress corrosion cracking, beginning with pitting holes in the rolled-in tube zone. The formation of Cu_2O covering films outside and on the walls at the pitting points is always present in conjunction with dissolution in the pitting root. The lowest stress limit necessary for the formation of cracks is reached at the dislocation congestions in the pitting root subsequent to macrostructural slipping, because at that point there is a summation of strains due to operating pressure and to the natural stresses evoked by the rolling-in process.

It is not surprising that stress corrosion cracking can be produced with ammonia-less NaCl solutions on stressed samples of CuZn28Sn, if at the same time conditions conducive to pitting prevail. Given a co-existence of Cu, CuO and CuOI in a 0.1 M NaCl solution with $\text{pH} = 4.8$, the equilibrium potential of a pitting spot lies between 0.25 and 0.27 V_{H} . These are values which can lead, after several hundred hours, to stress corrosion cracking.

For the most part, the transcrystalline transverse cracks in the transition zones remain approximately in the middle of the tube wall. One explanation for this is the entry into the seemingly neutral deformation fibre, at which the intrinsic strains transmute to compressive strains. We consider that only very few incipient cracks become through-cracks, thus causing leakage, the being that the additional tensile stresses leading to a complete break-through are missing.

Apart from the already mentioned transverse cracks in the rolling-in transition zones, especially under microscopic study with greater magnifications, longitudinal incipient cracking patterns can be discovered in the conical bulging zone of the rolled-in ends. These patterns are also due to stress corrosion cracking under introduced tangential tensile strains. Such hairline cracks hardly reach a depth of 100 microns and are therefore harmless.

A consequence to be drawn from what has been said concerning stress corrosion cracking in the rolling-in area, a practicable remedy is – as in the case of pitting corrosion – an improvement in the quality of the covering film.

EROSION CORROSION [22 to 24]

The demand for improved resistance to erosion corrosion of copper-base heat exchanger materials in cooling water circuits has led to the development of special aluminium brass and ferrous Cu-Ni alloys.

All according to the method of investigation, testing conditions and mode of interpretation, heavily fluctuating intervals for the permissible cooling water flow rates with respect to the individual materials are quoted. Such values are only of a tentative character since, in the individual case occurring in practice, varying ionic water composition, changing concentration and form of air bubbles and solids in the cooling water, fluctuating temperatures, as well as component-dependent flow patterns, are co-responsible for the mechanical-chemical behaviour.

The prevalent idea is that erosion corrosion damage occurs when the rate of covering film disintegration exceeds the new building-up rate of the covering film. After such incubation phases, which determine the useful life, the actual erosive reduction of the bare tube proceeds up to the complete break-through. This means that the

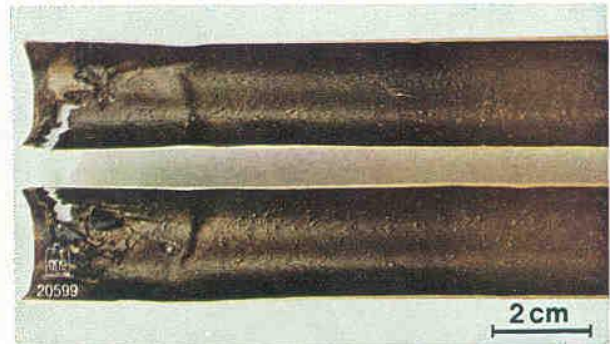


Figure 14. Erosion corrosion at the cooling water inlet end of a condenser tube (CuZn28Sn) caused by heavy intrusion of sand.

erosion strength, given constant flow conditions, is a direct function of the covering film's constitution. The covering film structure and its restorative capacity are narrowly tied up with the material in respect of the copper alloys here under review. In aggressive cooling waters, the build-up of the covering film is – as already said – at least equally dependent on the conditions of the medium during the build-up phase. Hence, the case may well arise in which an alloy (for example: CuNi30Fe), which can actually be used with higher flow rates, may fail (shallow pitting influenced by erosion) as compared with a lower-classed alloy (for example: CuZn28Sn). We thus attach little importance to the classification of alloys according to permissible flow rates with aggressive cooling waters.

The cases of damage arising from erosion corrosion, as investigated by us, are confined to the inlet zones of the first and second water passes, to the small-surface erosive reductions in the free tube lengths, and to the effect of the flow on shallow pitting locations. Identical damage was observed on tubes with a deficient protective film, i.e. low resistance of the covering film to polarisation at estimated average flow rates around 2.0 m/sec. The causes recognized as being responsible for the erosion extending up to 10 cm in the tubes were the sporadic intrusion of sand (Fig. 14) resp. heavy incidence of air bubbles on account of the rise in the cooling water temperature in the summer months. Under such conditions, there is said to be a helical flow turbulence at the tube inlet.

No explanation has been found for the causes underlying the erosive corrosion points which are distributed at



Figure 15. Erosive corrosion point in the free tube length (CuZn28Sn).

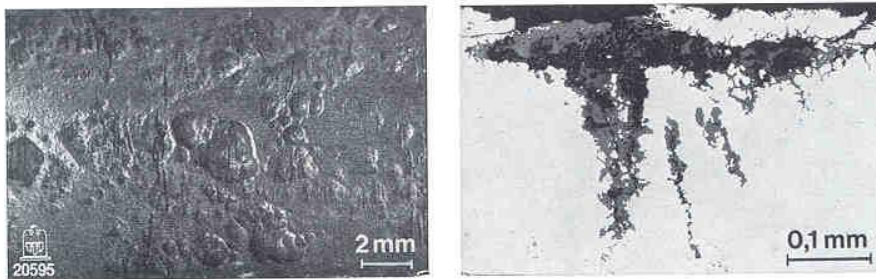


Figure 16. Low-cycle elongation fatigue cracks in an oil cooler tube (CuZn20Al) originating from corrosion pitting.

random along the free tube lengths. It can be assumed that solids have been temporarily held up at those points, thus interfering with the normal turbulence of the Reynolds type (Fig. 15).

One practicable way of protecting heat exchanger tubes from erosive corrosion is the building-up of extraneous oxide covering films in view of the limited possibility of influencing the natural oxide covering films.

FATIGUE CRACK CORROSION [25, 26]

Fatigue crack corrosion (corrosion fatigue) – characterised by transcrystalline cross-cracks in condenser and cooler tubes, can occur basically under alternating mechanical loads with tensile stress components using any cooling water and in any material. All according to the form of the alternating load, distinction is made between fissures arising under low-cycle stress changes of small amplitude (low-cycle corrosion fatigue) and cracks developing under vibrational loads of high frequencies and amplitudes.

With regard to the formation of low-cycle corrosion fatigue cracks, it is assumed that the material is in the active condition, at least at the cracking point of origin. There appear several parallel initial cracks which begin in wedge-

like fashion and become finer towards the ends of the cracks. They are very similar in form to stress corrosion cracks, so that a similar originating mechanism can be pre-supposed. Cracks of this kind are often observed in oil cooler pipes in the primary water circuit and develop mainly from pitting corrosion points (Fig. 16). It is evident that in such cases the alternating load appears in the form of temperature shocks after numerous operations of the coolers.

Fatigue corrosion cracks which occur under high stress frequencies can also appear in tubes with a completely passive covering film. Often, only one crack running as a sharp incision into the material is observed (Fig. 17). At the breaking surface of such cracks, isolated interference bands can be recognised as a typical feature of alternating stress. Occasionally but rarely, damages resulting from such a cause can be seen on domes and tubes from steam admission zone where there is an intensive surge current resulting from bypass resp. over-production steam.

DEALLOYING [27 to 33]

Dealloying of the layer and plug types are special forms of uniform corrosion and pitting which lead in all cases to augmentation of metallic copper at the corrosion points. Examples of this are provided by the well-known dezincification of brass, the denickelisation of CuNi alloys, as well as the de-aluminizing of CuAl alloys. Whilst the layer type of this selective corrosion can practically no longer be observed today on account of the arsenic inhibiting of the special brasses, the plug type with remarkable dissolution rates in the three mentioned alloy groups is not uncommon.

The basic differences in the explanations which have persisted for decades with regard to the effective mechanisms are resolved into two standpoints which seem to be diametrically opposite. Whilst the one standpoint assumes that the entire alloy first dissolves in the proportion of the alloy elements with subsequent re-precipitation of the purer copper component (Mechanism I), the other (theory speaks of an exclusive dissolution of the more impure alloy components Zn, Ni resp. Al, whereby a microporous surface layer of the purer copper metal with the structural remant of the original alloy (Mechanism II) remains. In the last few years there has been an approximation of the two standpoints to the extent that both mechanisms can ensue in accordance with the external conditions of the electrolyte composition and in keeping with the no-load potential (Fig. 18). A first estimation of the theoretical possibilities involved in the dealloying of monophasic copper alloys can be obtained by

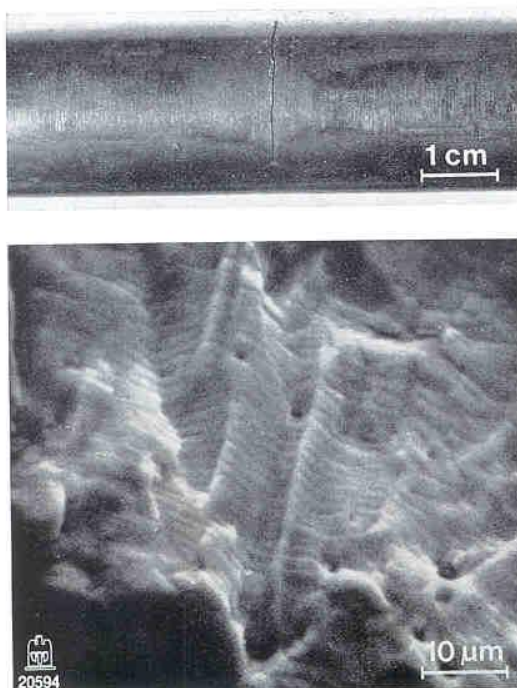


Figure 17. Fatigue corrosion crack in a tube (CuZn28Sn) from the steam admission zone between baffle plates.

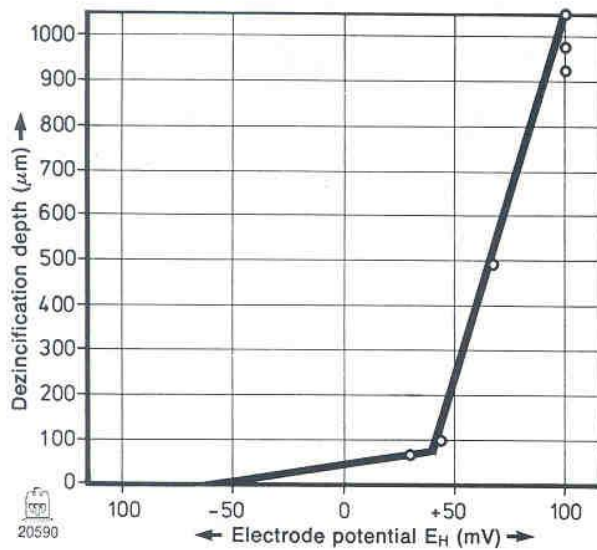


Figure 18. Dezincification depth of CuZn30 in a solution of CuCl_2 (5 g CuCl_2/l , 11 g HCl/ltr) after 48 hrs [29]

superimposing over the theoretical potential-pH charts for the participating alloy elements Cu, Zn, Ni the experimentally derived potential-pH charts for the alloys under review (e.g. Cu-Zn, Cu-Ni) in chloride solutions [32]. In such observations, the variations of potential caused by alloy and solution activities, coupling processes and covering film formation are disregarded.

Exclusively selective dissolution of the more impure components Zn and Ni is possible with corrosion potentials lying above the dissolving potentials of Zn and Ni and below the precipitating potentials of Cu (Fig. 19). In the case of alpha brass, the range is from + 0.2 to - 0.94 V_H , whereby the values depend to a small degree on the ion concentrations in the solution (thermodynamically explicable dealloying range).

Above the precipitating potential of copper, the ionisation of Zn and Ni, and the simultaneous dissolving of the Cu as CuCl_2 , Cu^- , Cu^{++} , along with oxidation to Cu_2O , CuCl resp. $3\text{Cu}(\text{OH})_2 \cdot \text{CuCl}_2$ without selectivity can be anticipated. Preferred dissolution of Zn and Ni can only be expected in this range of potential if the competing anode reactions ensue at a rate deviating from that of the alloy composition (kinetically explicable dealloying range). As already mentioned, the latter is the case with all copper alloys (Zn-free and Ni-free Cu_2O topotactic covering films). Simultaneous dissolution of Cu, Zn and Ni, and re-precipitation of metallic copper on the same sample is, however, only possible if there is a difference in potential

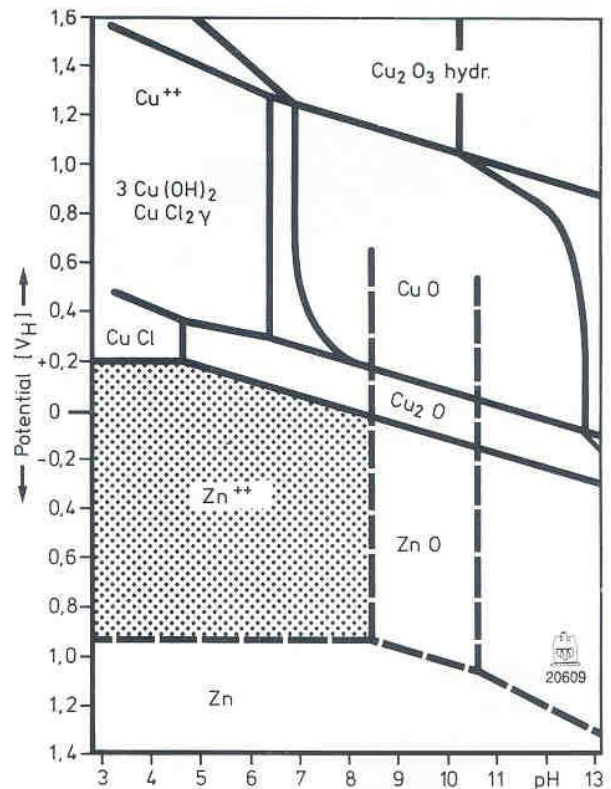


Figure 19. Simplified Cu-Cl- H_2O and Zn- H_2O chart (0.1 M Cl- and 10^{-6} M Cu and Zn ions).

between the location of dissolution and that of precipitation, this being the case, as already explained, between the anode spot (topotactic $\text{Cu}_2\text{O}/\text{alloy}$) and the cathode spot (epitactic $\text{Cu}_2\text{O}/\text{medium}$). All according to the absolute potential value, either re-precipitated copper on a Cu_2O covering film (Mechanism I) or metallic copper produced by selective dissolution in-growing into the alloy surface (Mechanism II), or both at the same time, will be encountered.

The thermodynamically explicable dealloying process through selective dissolution seems to ensue at a slow rate ($< 0.05 \text{ mm/a}$). It is therefore only possible to trace it in a metallographic laboratory test after long testing periods, whereas the kinetically explicable re-precipitating mechanism, with a suitable choice of potential and electrolyte, ensues much more rapidly. This may well create the impression that this process alone is relevant. In almost all the cases of industrial dezincification and denickelisation examined by us, we have been able to prove, by the use of more recent metallographical study

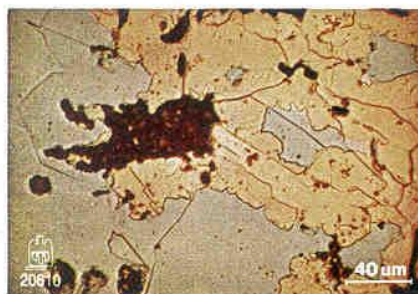


Figure 20a. Denickelisation of CuNi30Fe.

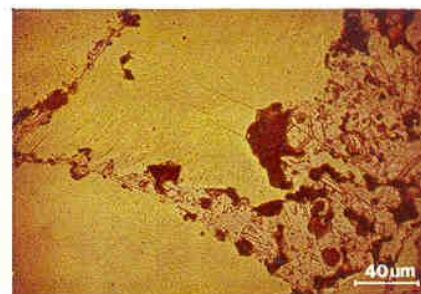


Figure 20b. Dezincification of CuZn28Sn.

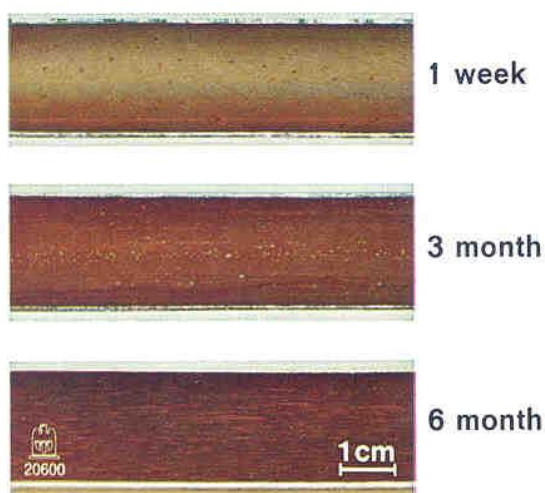


Figure 21. Change of colouring in condenser tubes (CuNi30Fe) through FeSO_4 injection.

methods, that selective dissolution mechanisms were operating (Fig. 20 a and 20 b). In all cases, these processes occurred underneath porous covering films which had been formed in cooling water with a high chloride content.

CORROSION PROTECTION BY EXTERNAL COVERING LAYERS [34 to 43]

From the aforesaid, it is clear that the failure of copper-alloy heat exchanger tubes due to pitting, stress corrosion cracking, erosion corrosion, fatigue corrosion cracking and dealloying can be mainly attributed to the inadequate quality of the natural oxide covering films formed in aggressive cooling waters. All the same, it shall not be denied that inappropriate — and often unavoidable — modes of operation as well as manufacturing faults, exert some influence on the degree of damage and on the time at which the said damage occurs.

Today it is hardly possible, economically, to obtain any substantial improvement in the passivity of the covering film through technical measures adopted in the alloying of copper material [48]. Economically also, the limits set for influencing the passivity of the covering films by constant treatment of the cooling water are very narrowly defined.

Of technical interest are the pre-treatment of new tubes with the object of producing natural oxide films free, as far as possible, from defective locations and withstanding corrosive attack at least for the duration of commissioning. First steps in this direction have been taken [35]. But it would be over-optimistic to assume that such

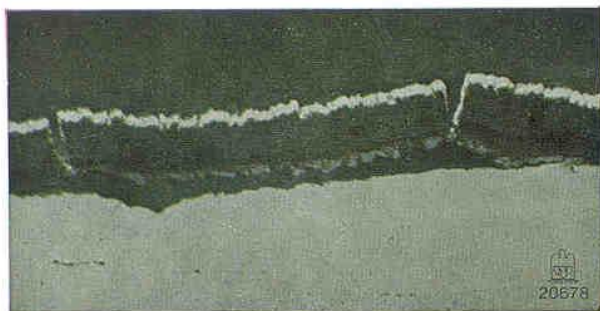


Figure 22. Hydrated FeO covering layer on a CuNi30Fe tube.

expressly pre-oxidized tubes could retain their full efficiency for the whole anticipated life of the tubing. We think therefore that in aggressive cooling waters the passivity of the natural oxide films must be considerably enhanced by external covering layers if we are to fully master the corrosive processes on copper alloys in aggressive cooling water circuits. It will be absolutely necessary to keep these layers intact throughout the entire operational period. The question as to whether these layers are of an oxidic, silicate or organic nature will be of less importance, but it is important that their electronic and ionic resistance is sufficiently strong to allow for their uniform and adhering distribution over the internal tube surfaces and to facilitate a reconstitution during operation.

Of the many conceivable and proposed systems, ferrous oxide layers have proved their efficiency in many respects. It is basically of no consequence whether these oxide layers are consciously produced, for example, by FeSO_4 injection or by making use of sacrificial anodes, or whether uncontrollably formed, for example, via the corrosion of steel tubes in the cooling water feed lines. The main thing is that the conditions of uniform distribution, good adhesion and reconstitution are maintained.

With regard to application of layers via FeSO_4 injection, several procedures have proved successful for continuous operation.

- Injection of 1 ppm Fe^{2+} in cooling water for the duration of 1 hour/day.
- Injection of the same concentration twice per day, but for $\frac{1}{2}$ -hour at a time.
- Continuous injection to values in the 10 ppb range.

What concentrations and sequences are chosen will depend, for example, on the organic matter and sulphide content in the cooling water. Especially during back-cooling, small quantities will be chosen as far as possible because of the formation of slime.

The injection of concentrated FeSO_4 solution (21 % FeSO_4 , 20° C) should be effected shortly before entry into the heat exchanger since, with longer dwell times, premature oxidation into flaking Fe(III) compounds will occur. In the case of large-size condensers, an additional injection into the return waterboxes can be expedient.

All according to the injection method, there will form after some weeks, on the inner surfaces of the tubes, brown, uniform layers of varying structure with thicknesses of 75 microns (Fig. 21). On continuous cleaning with sponge rubber balls or brushes, glossy reddish-brown films with a thickness of only very few microns appear, the thickness and roughness of which increases proportionally to the length of the cleaning interval. Automatic cleaning methods lead to a consolidation and homogenization of the external covering layers. There are differences of opinion with regard to the cleaning intervals for iron sulphate injection. Whilst there are some who aim at a firmly adhering and consolidated external protective layer with continuous cleaning, others are of the opinion that, on account of the formation of natural oxide films, a cleaning period of only one hour at a time can be vindicated.

The addition of the iron ensues via negatively or positively charged colloids of hydrated iron oxides, either under the influence of the electric field of the Cu_2O covering film with a positive sigma potential, or by electrolytic precipita-

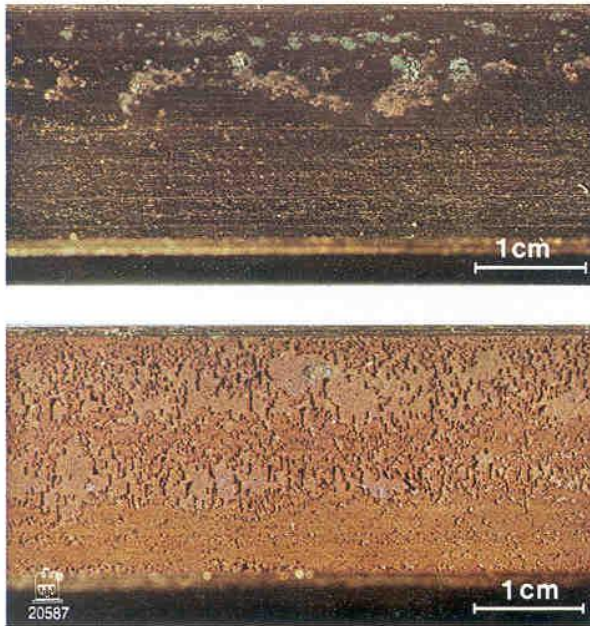


Figure 23. Condenser tubes before and after 1-year FeSO_4 injection.

tion on the cathode surfaces of the epitactic layer. Our own experiments bear out the latter assumption. It is therefore not expedient to inject directly onto pickled tubes, i. e. tubes deprived of their own natural covering film.

After a longer injection period, the layers show up in two lamellae (Fig. 22) on the metallographic picture. Over the natural Cu_2O covering film is a homogenous, closely-meshed layer of ferrous oxide, the crystalline content of which consists of gamma- FeOOH (lepidocrocite). In isolated cases, FeCuO_2 (delafossite) has also been radiographically diagnosed. According to the results obtained under electron microscope analysis, this hybrid oxide seems to occur as a thin intermediate layer to which adhesion-enhancing properties are ascribed.

The external ferrous oxide layers can be applied to all condenser tube materials, including austenitic CrNi steels and pure titanium. There are indications of differences in the adhering properties. Iron oxide layers have been successfully applied not only to brandnew

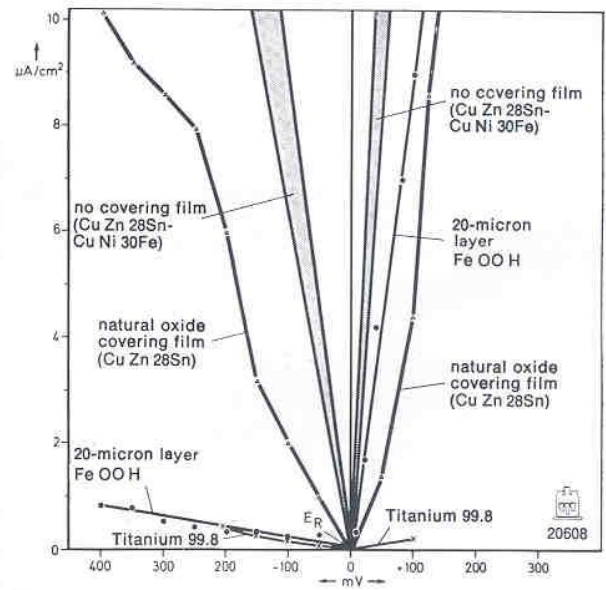


Figure 25. Potentiostatic polarisation graphs of industrial tubes in a 3% NaCl solution close to the no-load potential.

tubes, but also to tubes already damaged by pitting corrosion and erosive corrosion (Fig. 23).

In the case of injection with iron sulphate, the addition must be carried out throughout the entire operating period and, to an increased degree, after standstill because, for example, the layers chip and split on drying and peel off in some places (Fig. 24).

MEASURING THE STABILITY OF PROTECTIVE LAYERS [44, 45].

The objective appraisal of layer quality on copper alloys is important with respect to the general and selective behaviour of these materials under corrosion. The metallographical and visual methods of examination give only rough indications as to their properties and behaviour. On the other hand, an electro-chemical method enables the electronic and ionic resistance resp. the penetration polarisation of the anodic and cathodic reactions to be determined. In test sample tubes filled with a 3.4% NaCl solution, cathodic and anodic polarisation graphs are plotted up to a maximum current density of 10 microamps/

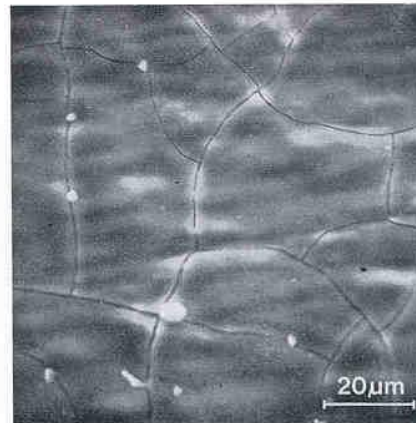
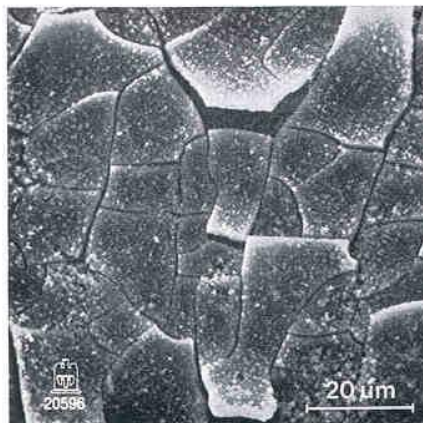


Figure 24. Oxide layers on condenser tubes injected with FeSO_4 , split and chipped on drying.

cm² (Fig. 25). The risings of the cathodic curves are directly proportional to the electronic resistance, whilst the risings of the anodic curves correspond with the ionic resistance.

Particularly striking is the high value of the electronic surface resistance in the external iron oxide layers (e.g. 580 mΩ/cm²) as against pickled tubes (8 mΩ/cm²) and defective natural films (11 to 15 mΩ/cm²). The influence of the external oxide layers on the ionic resistance is less pronounced. On the other hand, the natural oxide films seem to be of importance.

The salient feature of the method applied is that the measurement can be taken quickly, with a minimum of time and expense, and with the use of standard commercial components. As the tests were carried out on tubes which had been dismantled from plant condensers, there would seem to be no objection to applying this obviously reliable method to already assembled tubes. In this way, it would be possible to determine quantitatively by adequate measuring results the quality of covering films developed in operation, and to trace further progress. Pure titanium tubes have a special status, since their extremely high electronic and ionic resistances in the pickled as well as in the operationally passivated condition, are equal by virtue of their stable passivity. Opposed to the outstanding corrosion and erosion strength of pure titanium, under the cooling water conditions here in question, is the relatively high price of, for example, straight bead welded tubes which have, however, meanwhile drawn level with CuNi30Fe tubes in respect of the costs (wall thickness ratio 1:2).

SUMMARY AND CONCLUSION

The general and selective corrosion behaviour of copper alloy heat exchanger tubes is decisively influenced by the stability of the covering layers. In aggressive cooling waters, this layer passivity is not sufficient to prevent corrosion with certainty. The only guaranteed unproblematic method would seem to be the application of external layers (e.g. hydrated iron oxide films). The choice of tube alloy is of secondary importance with regard to cooling water corrosion, providing that the homogeneity, the adhering property and the density of the external covering layers are comparable. In the light of present-day considerations, we recommend the choice of CuZn28Sn for condensers on account of its enhanced resistance to pitting corrosion, and of CuZn20Al because of its enhanced resistance to erosive corrosion. In all cases, iron sulphate injection with continuous tube cleaning must be maintained right from the start.

Pure titanium is economically justified for tubing in the air suction zone of the condensers and auxiliary coolers.

LITERATURE

Comprehensive surveys

- [1] Nothing, F. W.: Korrosion, Ribbildung und Erosion an der Außenfläche von Kondensatorrohren aus Kupferlegierungen. Metall 10 (1956), S. 520-523 und 1033-1038.
 - [2] Bird, D. B., and Moore, K. L.: Brackish Cooling Water Versus Heat Exchangers. Materials Protection, Okt. 1962, p. 70-77.
 - [3] Splittgerber, E., and Börsig, F.: Schäden an Kondensatoren und Oberflächenkühlern. Der Maschinenschaden 37 (1964), S. 213-226.
 - [4] Matthewman, W., and Evans, G. J.: Corrosion in Power Station Condensers. Corrosion Technology, July 1964, p. 15-17.
 - [5] Fink, F. W.: Alloys for Sea Water Conversion. Copper-Base Alloys for Heat Exchange Equipment. Materials Protection May 1967, p. 40-43.
 - [6] Eichhorn, K.: Kondensatorrohre aus Kupferwerkstoffen. Richtlinien für Werkstoffauswahl und Betriebsbedingungen. Werkstoffe und Korrosion 21 (1970), S. 535-553.
 - [7] Held, H. D.: Kühlwasser, Kap. 4-6. Vulkan-Verlag, Essen 1970.
 - [8] Allianz-Handbuch der Schadenverhütung, 5.2. Kondensationsanlagen. S. 185-197, Allianz Versicherungs-AG, München 1972.
- ##### Uniform corrosion
- [9] Kruger, J.: The Oxide Films Formed on Copper Single Crystal Surfaces in Pure Water. I. Nature of the Films Formed at Room Temperature. II. Rate of Growth at Room Temperature. J. Electrochem. Soc. Vol. 106 (1959) p. 847-853; Vol. 108 (1961), p. 503-509.
 - [10] Leidheiser, H.: The Corrosion of Copper, Tin and their Alloys. Part Oxidation, p. 28-50. John Wiley and Sons, Inc. New York 1971.
- ##### Pitting corrosion
- [11] May, R.: Some Observations on the Mechanism of Pitting Corrosion. J. Inst. Met., Vol. 82 (1953/54), p. 65-74.
 - [12] Muysier, J. V., Pourbaix, M., Laer, P. V.: Electrochemical Nature of the Pitting Corrosion of Copper in Water and Aqueous Solutions. Rapport Technique CEBELCOR RT. 127, Mai 1965.
 - [13] Lucey, V. F.: Mechanism of Pitting Corrosion of Copper in Supply Waters. British Corrosion J. Vol. 2 (1967), p. 175-185.
 - [14] Pourbaix, M.: Bestimmung und Anwendung von Gleichgewichtspotentialen. Werkstoffe und Korrosion 20 (1969), S. 772-784.
 - [15] Retief, R.: Condenser Tube Corrosion Problems. Experienced in the Inland Power Stations of ESC. The Nat. Inst. Engg. Vol. 9 (1970), p. 1-10.
 - [16] Szklarski-Smialowska, Z.: Review of Literature on Pitting Corrosion, Published Since 1960. Corrosion 27 (1971), p. 223-233.
- ##### Stress corrosion cracking
- [17] Perkins, R. N.: Stress Corrosion Cracking. Metals Rev. Vol. 9 (1964), p. 201-260.
 - [18] Logan, H. L.: The Stress Corrosion of Metals. John Wiley and Sons, New York 1966.
 - [19] Graf, L., and Wittich, W.: Untersuchungen von Sonderfällen der Spannungsrißkorrosion bei homogenen, nicht übersättigten Mischkristallen und der hierbei auftretenden elektrochemischen Prozesse. - Teil II: Weitere Untersuchungen zur Spannungsrißkorrosion des Messings. Werkstoffe und Korrosion 17 (1966), S. 471-476.
 - [20] Scully, J. C.: The Mechanical Parameters of Stress-Corrosion Cracking. Corrosion Sci. Vol. 8 (1968), p. 759-769.
 - [21] Engell, H. J., and Speidel, M. O.: Ursachen und Mechanismen der Spannungsrißkorrosion. Werkstoffe und Korrosion 20 (1969), S. 281-300.
- ##### Erosion corrosion
- [22] Page, G. G.: Some Operating Conditions Influencing Attack of Nonferrous Tubular Condenser and Heat-exchange Equipment. First Intern. Congr. Metallic Corrosion, Butterworths London 1962, p. 613-618.
 - [23] Sick, H.: Die Erosionsbeständigkeit von Kupferwerkstoffen gegenüber strömendem Wasser. Werkstoff und Korrosion 23 (1972), S. 12-18.
 - [24] Loss, C., und Heitz, E.: Zum Mechanismus der Erosionskorrosion in schnellströmenden Flüssigkeiten. Werkstoffe und Korrosion 24 (1973), S. 38-48.
- ##### Fatigue corrosion cracking
- [25] Dies, K., und Jung-König, W.: Korrosionswechselfestigkeit von Kupfer und Kupferlegierungen, insbesondere von Mehrstoff-Aluminiumbronzen. Werkstoffe und Korrosion 17 (1966), S. 462-468.
 - [26] Spahn, H., und Steinhoff, U.: Vergleichende Betrachtungen zur Spannungs- und Schwingungsrißkorrosion. Werkstoffe und Korrosion 20 (1969), S. 733-749.
- ##### Dealloying
- [27] Feller, H. G.: Über die selektive Korrosion der Kupfer-Zink-Legierungen. Z. Metallk. 58 (1967), S. 875-885.
 - [28] Heidersbach, R.: Clarification of the Mechanism of the Dealloying Phenomenon. Corrosion 24 (1968), pp. 38-44.
 - [29] Langenegger, E. E., and Robinson, F. P. A.: A study of the Mechanism of Dezincification of Brasses. Corrosion 25 (1969), pp. 59-66.
 - [30] Pickering, H. W., and Byme, P. J.: Partial Currents During Anodic Dissolution of Cu-Zn Alloy at Constant Potential. J. Electrochem. Soc. Vol. 116 (1969), pp. 1492-1496.

- [31] Rothenbacher, P.: Zur Entzinkung von rekristallierten und statisch belasteten Kupfer-Zink-Legierungen – mit 30 At-% Zink. *Corrosion Sci.* 10 (1970), pp. 391-400.
- [32] Verink, E. D., and Heidersbach, R. H.: Evaluation of the Tendency for Dealloying in Metals Systems: Localized Corrosion – Cause of Metal Failure. ASTM Spezial Technical Publication 516, 1972, pp. 303-322.
- [33] Heidersbach, R. H., and Verink, E. D.: The Dezincification of Alpha and Beta Brasses. *Corrosion* 28 (1972), p. 397-416.
- Induced and natural oxide films
- [34] Bostwick, T. W.: Reducing Corrosion of Power-Plant Condenser Tubing with Ferrous Sulfate. *Corrosion* Vol. 17 (1961), p. 12-19.
- [35] Sere, J., and Laureys, J.: Service Behaviour of Copper Alloy Tubes in Heat Exchangers. *Corrosion Sci.* 5 (1965), p. 135-155.
- [36] Lockhart, A. M.: Reducing Condenser Tube Corrosion at Kincardine Generating Station with $FeSO_4$. *Proc. Inst. Mech. Engr.* Vol. 179 (1965), p. 495-512.
- [37] North, R. F., and Pryor, H. J.: The Protection of Cu by Ferrous Sulfate Additions. *Corrosions Sci.* 8 (1968) p. 149-157.
- [38] Ferrous Sulfate Treatment to Prevent Corrosion of Condenser and Heat Exchanger Tubes. Yorkshire Imperial Metals. Technical Bulletin TB/7, 1970.
- [39] Ionilli, E.: Mechanism of Protective Film Formation on Cu-Alloy Condenser Tubes with $FeSO_4$ -Treatment. *Corrosion Sci.* 10 (1970), p. 157-163.
- [40] Zen-ichi Tanabe: Effect of Ferrous Ion on Corrosion of Condenser Tube Alloys. Sumitomo Light Metal Technical Reports Vol. 11 (1970), p. 42-48.
- [41] Shiro Sato, Koji Nagata and Akio Ogiso: Effect of Sponge Ball cleaning on the Corrosion of Condenser Tubes. Corrosion by Clean Sea Water (Rep. 1); Corrosion by Polluted Sea Water (Rep. 2); Sumitomo Light Metal Technical Reports Vol. 11 (1970), p. 1-20; Vol. 13 (1972), p. 3-12.
- [42] Nosetani, T.: Der Einfluß verschiedener Faktoren auf das Betriebsverhalten von Kondensatorrohren aus Kupferlegierungen. Sumitomo Light Metal Technical Reports 12 (1971), S. 11-26.
- [43] Pearson, C.: Role of Iron in the Inhibition of Corrosion of Marine Heat Exchangers – A Review. *Br. Corrosion J.* 7 (1972), p. 61-68.
- Electro-chemical measurements of covering film stability
- [44] North, R. F., and Pryor, H. J.: The Influence of Corrosion Product Structure on the Corrosion Rate of Cu-Ni-Alloys. *Corrosion Sci.* 10 (1970), pp. 297-311.
- [45] Giuliani, L., and Bombara, G.: An Electrochemical Study of Copper Alloys in Chloride Solutions. *Br. Corrosion J.* 5 (1970), p. 179-183.
- Tube materials
- [46] Bailey, G. L.: Copper-Nickel-Iron Alloys Resistant to Sea Water Corrosion. *J. Inst. Met.* 79 (1951), p. 243-252.
- [47] Stewart, W. C., and Laque, F. L.: Corrosion Resisting Characteristics of Iron-Modified 90:10 Cupro-Nickel Alloy. *Corrosion* 8 (1952), p. 259-277.
- [48] Shiro Sato: Development of Copper Alloy Condenser Tubes Resistant to Polluted Water. *Proc. Fourth Int. Congr. Metallic Corrosion Nat. Ass. Corr. Engrs.* 1972, pp. 792-802.
- [49] ASTM-Designation B 338-65: Standard Specification for Seamless and Welded Titanium Tube for Condensers and Heat Exchangers.
- [50] Feige, N. G.: Titanium Tubing Proves Value in Estuary Application. *Power Engineering*, Jan. 1973, p. 52-54.