

A Comparative Study of the Corrosion Behaviour of Some Plain and Modified Brasses

Md. Mohar Ali Bepari *
Md. Serajul Islam **

ABSTRACT

Plain brasses with 30% and 40% zinc contents and the corresponding modified brasses obtained with the substitution of 1% zinc by tin were subjected to the action of seven different media at 60°C. The kinetics of corrosion and associated aspects together with macro investigations were carried out with the specimens.

It was observed that addition of tin improves the corrosion resistance of both the types of brasses. The more concentrated alkaline solution causes the loss of both copper and zinc from the brasses, but copper is subsequently redeposited upon the alloy surface. The corrosion rate in this medium is more than about three orders of magnitude higher as that in all other media. Tap water is about 2-3 times more corrosive as compared to sea water or river water.

INTRODUCTION

Brass has been known for a long time as an important engineering material. Many machine parts such as large bolts and nuts, pins and spindles, sockets, rivets, radiator cores and tanks, reflectors, springs, bullet jackets, fire extinguishers, condensers, evaporators, rudders, propeller shafts, heat exchanger tubes and plates, sanitary and marine fittings, etc. are made of brasses (1-4). Some of these parts, particularly those used in marine environments, should possess sufficient resistance to corrosion in sea water (4-7).

Many Cu-Zn alloys in a major part corrode in water by a process called dezincification in which brass in dis-

solved and copper is reprecipitated in situ as a spongy mass. Dezincification is one of the well-known de-alloying processes by means of which brass loses its valuable physical and mechanical properties leading to the total failure of the structure. The literature survey on the mechanism of de-alloying (8) in general and dezincification (9) in particular provides a good basis for understanding various aspects of dezincification and its inhibition. The work of Abrams(10) in 1922, dealing with critical analysis of the various environmental factors on dezincification, contributed a basic understanding of the problem. Due to its industrial significance, dezincification has been an active field of research and attempts (11-18) have been made to resolve

* Department of Metallurgical Engineering, BUET, Dhaka 1000, Bangladesh

the controversy over the mechanism of the process. Dezincification generally occurs in waters of low temporary hardness and high chlorine content and can result in perforation of fittings or blockage due to the deposition of bulky meringue like zinc corrosion products (19). Soft waters specially may lead to corrosion failures from localized dezincification of the brasses containing more zinc such as Muntz metal (60% Cu, 40% Zn), non-inhibited aluminium brass (76% Cu, 22% Zn, 2% Al) and yellow brass (70% Cu, 30% Zn) containing no dezincification inhibitor.

A reduction in the zinc content of the Cu-Zn alloy decreases its susceptibility to dezincification. Brasses, for example, containing more than 85% copper are practically immune. The addition of tin or arsenic to the plain brasses containing more than 15% zinc usually is quite effective in slowing or inhibiting the dezincification reaction in fresh water and in sea-water. When 1% zinc is substituted from Muntz metal and yellow brass by tin then the modified brasses are known as naval brass and admiralty brass respectively.

This investigation was undertaken in order to make a comparative study on the effect of about 1% tin addition on the corrosion behaviour of a 70/30 brass and a 60/40 brass in different corrosion media such as sea water, river water, tap water and salt and alkali solutions of varying concentrations.

EXPERIMENTAL PROCEDURE

Four brasses were prepared. The composition in weight percentage are presented in Table 1. The brasses were made in a gas-fired pit furnace. First of all metallic copper was melted under an atmosphere of charcoal and when the metal was sufficiently fluid, the crucible was taken out of the furnace and zinc and tin were added to it. It was then stirred continuously for a while and poured into sand moulds. In order to compensate for the loss of zinc due to volatilization during mixing, about 5% excess of the amount of zinc required was added. 3 to 4 castings of approximately 25mm x 13mm x 150mm size were made.

Specimens of about 24mm x 12mm x 3mm were cut out by a milling cutter taking care that the faces of the rectangular discs are parallel. The faces of the discs were then made exactly parallel by a surface grinding

machine. A small hole of about 1/16" in diameter was drilled at one corner of each disc. The specimens were then polished very carefully in a series of emery papers of increasing fineness upto 2/0 grade paper.

The surface area of each of the polished specimens was calculated and the weight of each of them was also taken in a semi-micro balance.

Seven different media of corrosion namely, river water*, sea water*, tap water, 5% NaCl solution, 1% NaCl solution, 5% NaOH solution and 1% NaOH solution were used in the present study. 400ml of each of these solutions was taken in seven different lots each consisting of four different 500ml conical flasks. One specimen from each of the four types of brasses was dipped into each flask of a particular medium with the help of a plastic string. A funnel was also provided at the top of each flask to minimise evaporation of the solution. These flasks were then maintained at 60°C on a hot plate. The specimens were withdrawn from the solutions at regular intervals, cleaned thoroughly with running water and acetone and then dried in a drier at 110°C for about an hour. These corroded specimens were then weighed in a semi-micro balance. The surface appearance of these specimens was studied by visual and macro examinations and any peculiarity/distinguishing features recorded. The specimens were again dipped into the solution and exposed to the corroding media for specified times and the cycle of operations repeated.

Necessary data were recorded after each cycle. It may be noted that any medium that was found to have been badly affected due to prolonged exposure was replenished by fresh solutions at suitable intervals.

RESULTS

The specific weight loss values, $\Delta W/A$, with time for each specimen of the four categories of brasses in seven different corroding media along with the initial weight and surface area of each were duly recorded and tabulated. Necessary graphs were then drawn from these data. Figures 1 to 4 represent these curves in which the weight loss (or gain) per unit area of specimen surface, called the specific weight change, has been plotted against time.

*River water has been collected from the Buriganga and sea water has been collected from the Bay of Bengal.

The corrosion kinetics of the 60/40 and of the 70/30 plain brass specimens in different media at 60°C have been shown in Figures 1 and 3 respectively. It is evident from these figures that in general, the specific weight loss values of these specimens rise sharply in the initial stage of the experiment for all these media. It may be noted, however, that although the curves for the 1% NaCl solution in both the figures represent an initial decrease in specific weight like the other specimens, but soon it assumes a negative slope, thereby indicating a continuous gain in subsequent specific weight change values.

The corrosion rates for all these specimens in all the different media finally attain constant or steady values as indicated by the curves. These values, together with those for the corresponding modified brasses have been shown in Table 2. It may be noted from figures 1 and 3 that in the initial stages (i.e. upto about 50 hours) the specific weight loss values for both the types of plain brasses in the 5% NaCl medium, in river water and in sea water are nearly identical except that for the 60/40 plain brass in sea water (which is much lower). Moreover, it will also be apparent from Table 2 that the steady-state corrosion rates for both the types of plain brasses are not much different in these three media, except that the rates for the 70/30 plain brass are only about one-half to one-fourth the rates for the 60/40 plain brass.

Table 2 also reveals that the steady-state corrosion rates of the 60/40 and of the 70/30 plain brasses in tap water are comparatively much higher than those in sea water and in river water. The effects of these media will be apparent from figures 5 and 6. It will be seen that the greater corrosion rate in tap water results in a complete removal of polishing marks from the surface of the specimen exposed to this medium, figure 5, whereas such marks are observed to have been largely retained on the other two relevant specimens, figure 6.

Figures 2 and 4 represent the corrosion behaviour of the two types of brasses which have been obtained through the replacement of 1% Zn by 1% Sn in the two plain brasses; the temperature of exposure, of course, remains the same as before (i.e. 60°C). It will be apparent from these figures, that for all of these media the specimens record a more or less sharp initial decrease in their specific weights and their corrosion rates subsequently attain more or less constant values.

It may be noted that in the initial stage of the experiments (i.e. upto about 50 hours) the specific

weight loss caused by the 5% NaOH solution is the highest amongst those caused by all other media for all the types of brasses. These values for this medium subsequently tend to decline for a while but ultimately increase to attain much higher steady-state values. It will also be noticed from Table 2 that there is little difference between the steady state corrosion rates of the specimens exposed to sea water and to 5% NaCl solution.

The effects of decreasing the concentration of the NaOH solution upon the brasses at 60°C were studied by exposing them to solutions of two different concentrations. It may be noticed from Table 2 that the concentration of the medium has a tremendous effect upon the corrosion rates of all the brasses. The steady-state corrosion rates are about 2000-4500 times in the 5% NaOH solution as that in the 1% NaOH solution. Moreover, it may also be noticed that for both the media, the corrosion rates of the plain brasses are somewhat higher than those of the modified brasses (about 1.5 times).

Variation in the concentration of the NaCl solution also produced variable effects upon the corrosion rates of the brasses. The 5% NaCl solution caused a continuous loss in specimen weight with increasing times of exposure for all the brasses. The 1% NaCl solution, on the other hand, at first caused loss in weight for the plain brass specimens (between 50-100 hours), but subsequently recorded a continuous gain in specimen weight upto the end of the experiment, thereby indicating that some adherent coating were being formed upon the specimen surface. The modified brasses, however, were affected in this medium in the usual way i.e. loss in weight was observed with increasing time of exposure. Table 2 reveals that the steady-state corrosion rates of the plain brasses in 5% NaCl solution are about 1.5 times those of the modified brasses.

DISCUSSION

It is observed that the final rates of attack upon all the brass specimens in the 5% NaOH solution are more than three orders of magnitude higher as compared to those in the 1% NaOH solution. This tremendously high rate of attack by the more concentrated solution was also apparent from the much deeper blue colour or greenish blue colour of the 5% NaOH solution than that of the 1% NaOH solution after a certain time of exposure. It is well known that zinc readily goes into solution in sodium

hydroxide forming soluble sodium zincate, and it is possible that the 5% NaOH solution should have a greater corroding effect upon the specimens than the 1% NaOH solution. The more concentrated solution (i.e. 5% NaOH solution), therefore, dissolves out more copper and zinc due to which it assumes a deeper blue or greenish blue colour. The surface of the specimen, therefore, assumes a bright golden colour in the initial stage. However, after a longer exposure, the surface gradually turns to a reddish or brick red colour. It has been reported (21) that zinc is preferentially dissolved out from the surface leaving the copper behind or both metals dissolve, but copper is subsequently re-deposited upon the surface of the metal. The brick-red colour of the deposit upon the specimen surface is obviously due to this re-deposition phenomenon.

Table 2 also indicates that the steady-state corrosion rates of the plain brasses in 5% NaCl solution are higher than those of the corresponding modified brasses which may be attributed to the presence of tin in them. It can also be noted that the solution is almost twice as corrosive upon the 60/40 plain brass as upon the 70/30 brass. The equilibrium diagram for binary copper-zinc alloys(20) indicates that 70/30 brass is a single phase α brass while 60/40 brass contains both α and β phases at room temperature. The higher rate of corrosion of 60/40 brass than that of 70/30 brass in 5% NaCl solution is thus clearly due to the heterogeneous nature of the higher-zinc brass than the single phase 70/30 variety.

On the other hand, the steady-state corrosion rates with both the plain 60/40 and the 70/30 brasses are almost identical in 1% NaCl solution. The same is also true with the corresponding modified brasses. Visual examination of the surfaces of the plain brass specimens after each exposure revealed some greenish deposits here and there. These deposits, as may be expected, retard the rate of corrosion in the plain brasses, and apparently being of an adherent nature, are responsible for the negative slopes of their corrosion curves. No adherent deposit was, however, observed to have formed on the modified varieties in this corrosion medium. The two kinetics curves, therefore, maintain a positive slope throughout the experiment.

It is also seen from Table 2 that for both tap water and river water, the steady-state corrosion rate of each of the plain 60/40 brass and of the plain 70/30 brass is about 4-5 times those of the corresponding modified brasses. At the same time, the steady-state corrosion rates of these

plain brasses are observed to be very high in tap water as compared to those in the river water. This fact is revealed from figures 5 and 6 which represent the surface appearances of the 60/40 plain brass specimens in tap water and in river water respectively. The relatively large amount of corrosion produced by tap water is indicated by the complete removal of the polishing marks from the surface of the particular specimen, figure 5, whereas such marks are more or less completely retained upon the surface of the specimen exposed to river water, figure 6. Exactly similar differences were noticed between 70/30 plain brass specimens dipped in tap water and river water. It may be noted from Table 2 that the steady-state corrosion rates in the former medium for both the kinds of the plain brasses are about 2.5-10 times those in the later medium. It seems possible that this comparatively higher rate of corrosion in tap water is due to the presence of dissolved chlorine or the corresponding free acids in the tap water, the disastrous effects of which are very much effectively counteracted by the presence of 1% tin in the modified varieties (a little more modified 70-29-1 alloy is thought to be somewhat more corrosion resistant than the other modified variety).

The steady-state corrosion rate in tap water of the 60/40 brass and that of the corresponding modified brass are about 2.5 times the rates of corrosion of the respective brasses in river water but those of the 70/30 brass and of the corresponding modified brass in tap water are about 10 times those in river water. This adverse effect of tap water, as already noted, is due to the presence of a large amount of dissolved chlorine in it. It is known that overhead tanks in residential buildings are frequently treated with bleaching powder.

CONCLUSIONS

The following conclusions may be drawn from the work done so far:

(1) Addition of small amounts of tin to the 60/40 and the 70/30 brasses considerably improves their corrosion resistance in almost all the media under investigation.

(2) Dezincification occurs in all varieties of the brasses subjected to the action of the more concentrated alkaline solution. Copper is also believed to be dissolved out but is subsequently re-deposited upon the specimen surface as a result of electrochemical action.

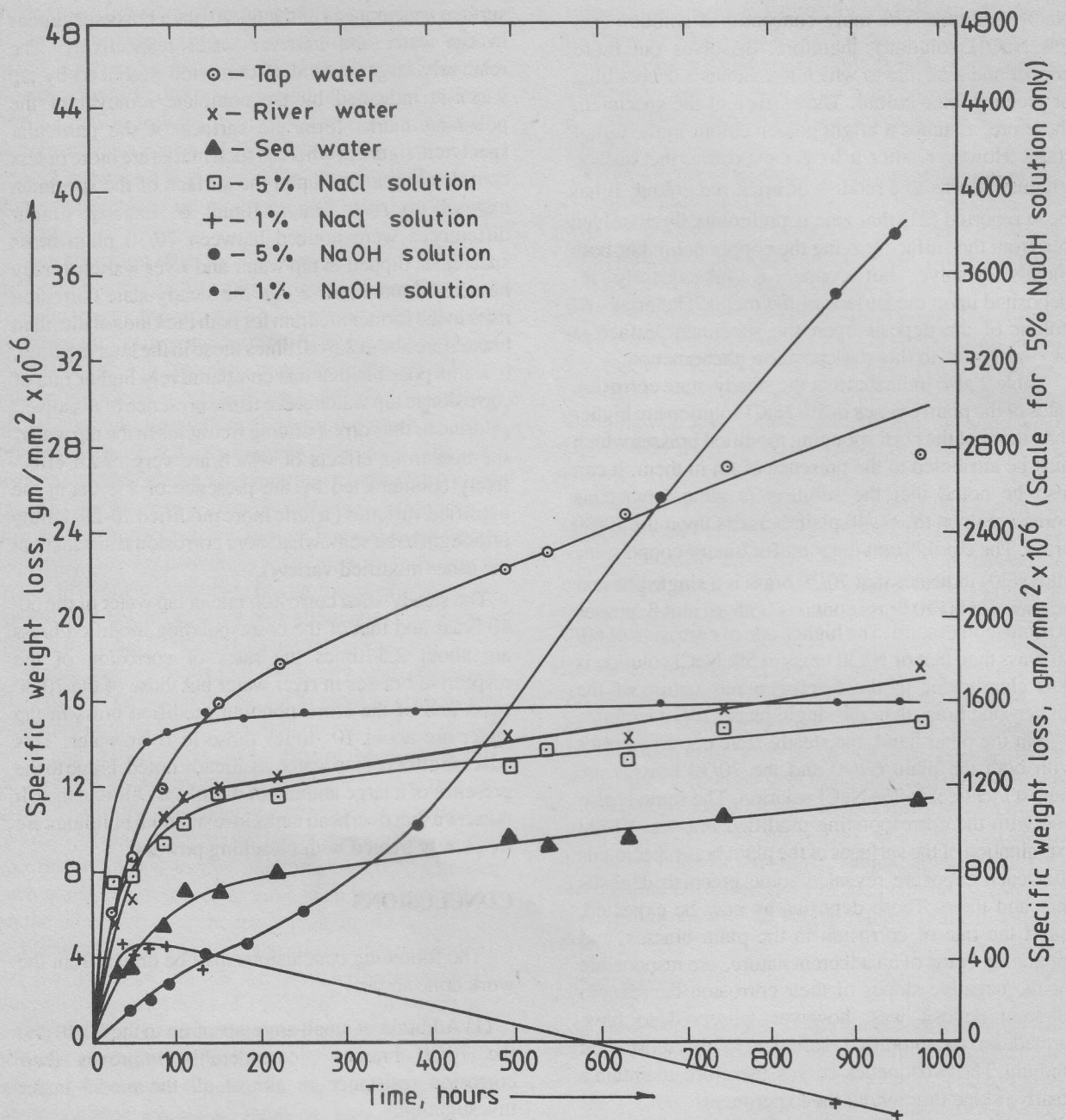


Fig.1 Variation of specific weight loss of 60-40 plain brass specimens with time in different media.

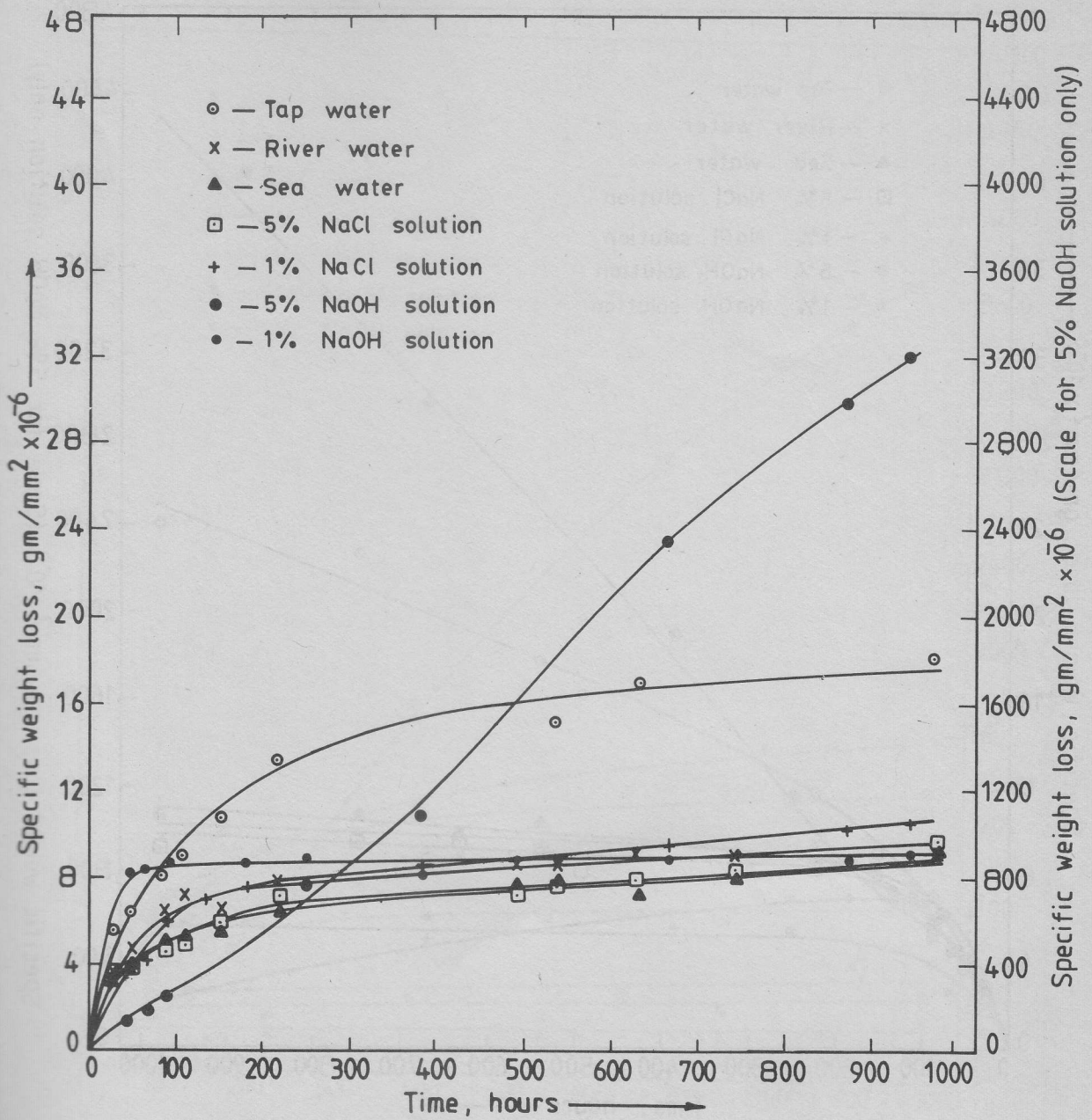


Fig. 2 Variation of the specific weight loss of 60-39-1 modified brass specimens with time in different media.

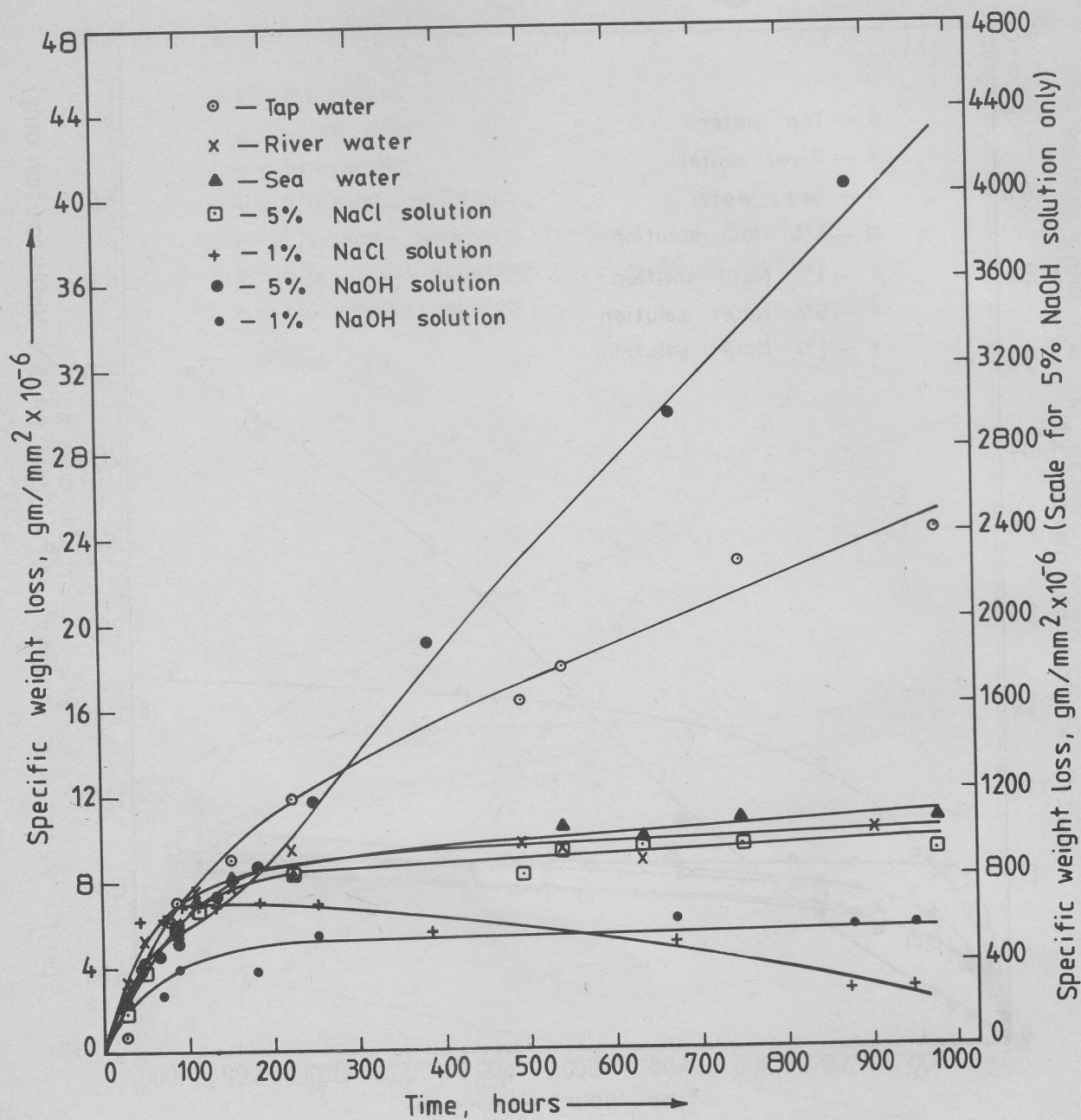


Fig.3 Variation of specific loss of 70-30 plain brass specimens with time in different media.

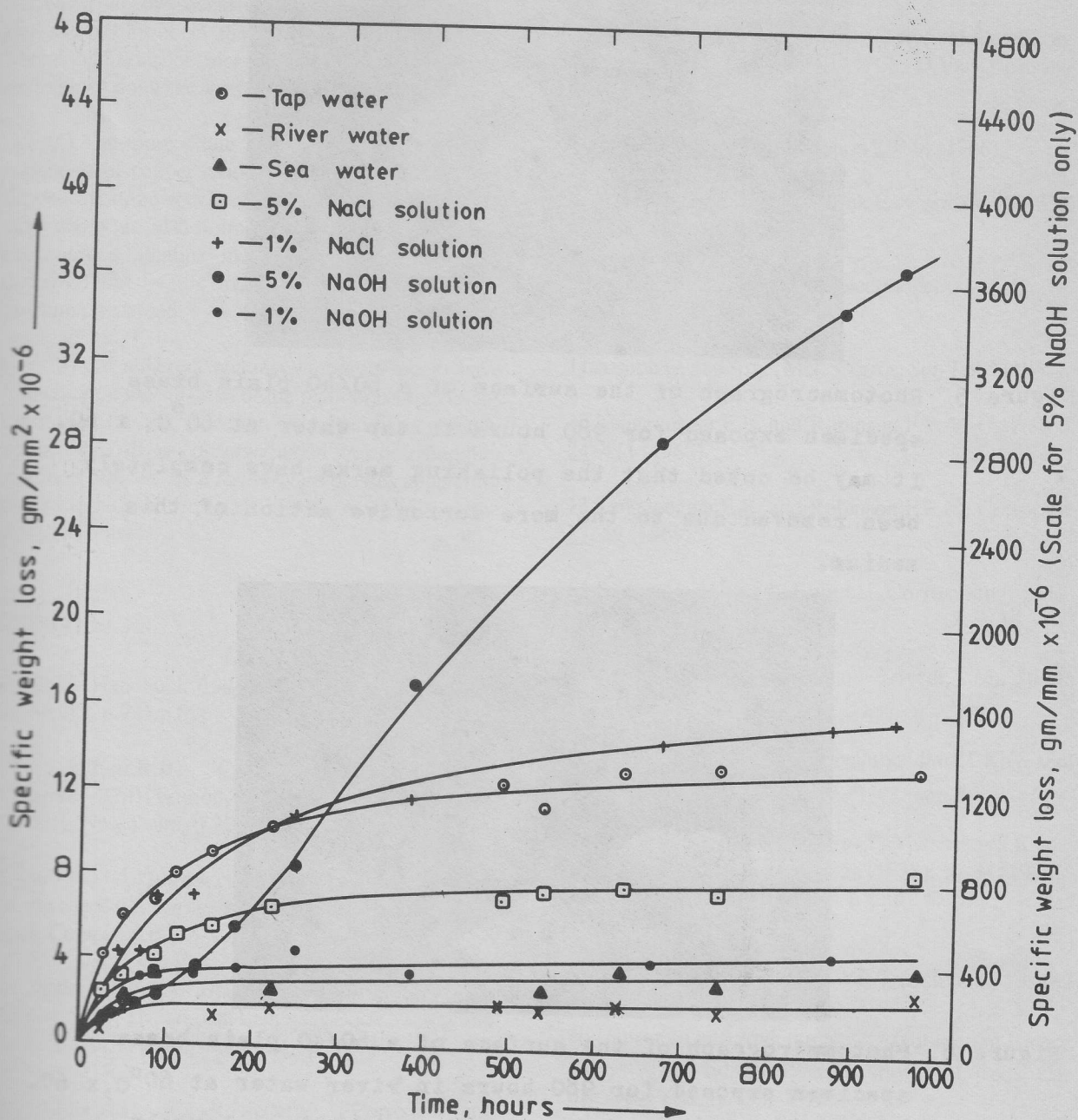


Fig. 4 Variation of the specific weight loss of 70-29-1 modified brass specimens with time in different media.

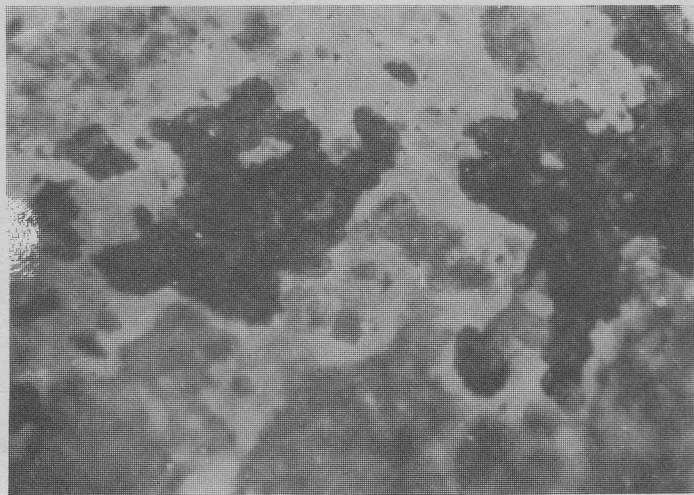


Figure 5 Photomicrograph of the surface of a 60/40 plain brass specimen exposed for 980 hours in tap water at 60°C, x 60. It may be noted that the polishing marks have completely been removed due to the more corrosive action of this medium.

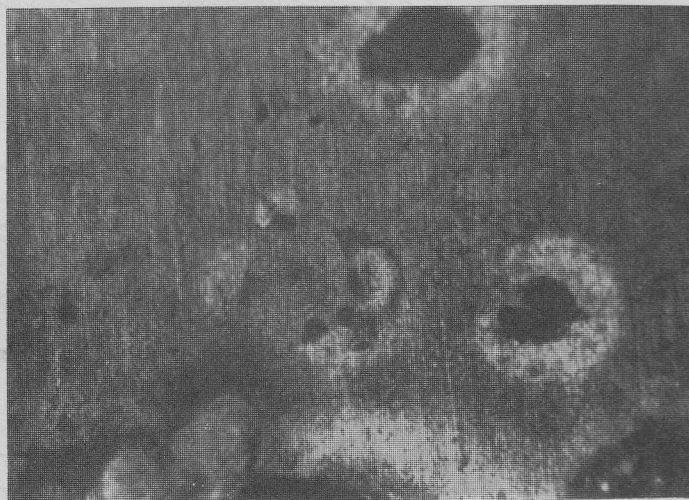


Figure 6 Photomicrograph of the surface of a 60/40 plain brass specimen exposed for 980 hours in river water at 60°C, x 60. Polishing marks may be observed to have been largely retained due to the less severe action of this medium. An identical surface appearance could be noticed with the specimen exposed to sea water.

(3) Tap water is found to have an abnormally high corrosive effect upon both the types of plain brasses, as compared to other media. This can probably be attributed to the occurrence of large amounts of dissolved chlorine in the medium. It is known that liberal additions of bleaching powder are made at intervals in domestic water supply systems.

(4) The more dilute alkaline solution causes the formation of copper oxide which appears as a black deposit upon the specimen surface. It is possible that such an oxide also forms in the case of the more concentrated alkaline medium but is subsequently dissolved out by the more corrosive action of the medium concerned.

(5) An adherent coating was observed to have formed upon the surfaces of the plain brass specimens exposed to 1% NaCl medium only. Peculiarly enough, no such deposit was observed upon the corresponding modified brasses. As a result, plain brasses apparently proved to be more resistant in this medium than the modified brasses.

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Table 1 Composition of the brasses

Material	% Composition	
	Nominal	Actual
(1) 60-40 Plain Brass	60 Cu-40 Zn	60.15 Cu-39.85 Zn
(2) 60-39-1 modified brass	60 Cu-39 Zn-1 Sn	59.95 Cu-39.05 Zn-1 Sn
(3) 70-30 Plain Brass	70 Cu-30 Zn	70.05 Cu-29.95 Zn
(4) 70-29-1 modified brass	70 Cu-29 Zn-1 Sn	70.06 Cu-28.88 Zn-1.06Sn

Table 2 Steady-state corrosion rates of the plain and modified brass specimens in different media at 60°C.

Corrosion medium	60-40 plain brass	60-39-1 modified brass	70-30 plain brass	70-29-1 modified brass
	Corrosion rate, mg/dcm ² -day (mdd)	Corrosion rate, mg/dcm ² -day (mdd)	Corrosion rate, mg/dcm ² -day (mdd)	Corrosion rate, mg/dcm ² -day (mdd)
5% NaOH solution	10.879x10 ⁻⁶	7.022x10 ⁻⁶	10.08x10 ⁻⁶	7.159x10 ⁻⁶
1% NaOH solution	2.40x10 ⁻⁹	1.524x10 ⁻⁹	6.751x10 ⁻⁹	3.998x10 ⁻⁹
5% NaCl solution	10.572x10 ⁻⁹	7.056x10 ⁻⁹	5.434x10 ⁻⁹	3.389x10 ⁻⁹
1% NaCl solution	-19.358x10 ⁻⁹	8.640x10 ⁻⁹	-17.332x10 ⁻⁹	10.824x10 ⁻⁹
Tap water	37.714x10 ⁻⁹	8.726x10 ⁻⁹	39.792x10 ⁻⁹	7.0001x10 ⁻⁹
River water	15.257x10 ⁻⁹	3.636x10 ⁻⁹	3.907x10 ⁻⁹	0.727x10 ⁻⁹
Sea Water	12.552x10 ⁻⁹	6.857x10 ⁻⁹	6.329x10 ⁻⁹	4.234x10 ⁻⁹