CHAPTER IV

RESULTS AND DISCUSSIONS

RESULTS AND DISCUSSION

Study of 'cooling waters' and the problems associated with them, though not either unrecognised or totally unexplored, is less paid attention to from the 'chemical' point of view, while its technological and engineering aspects are well explored. Strange though it may appear, the 'simpler' things as viewed from the common perspective, are the more difficult ones to manage and control. This dictum has relevance to the present study since the common view of a layman would be the one of just achieving 'cooling' by 'touch' and 'transfer' of energy with waters, which can be easily pressed into service as an abundantly available commodity that is so widespread. Even some well versed in the art and craft of applied sciences may miss the enormity of the problematic aspects of 'cooling waters treatment' at the first instance, the 'miserable' part of the entire operation is realized when (i) the supply of fresh water becomes a problem, (ii) the 'production' goes down on account of inefficiency of 'cooling' system and (iii) the problem of the disposal of the 'waters' assumes the nature of a serious task and creates legal hazards.

'Cooling water' may be explained as a sort of normal water channelised through a system with the view to bring down the temperature of another system (chemical) which would be the important step in the production of a material for which the factory or the manufacturing unit has been set-up. Such a system would involve 'exchange of energy', and with this 'exchange' business, get involved a number of aspects such as (i) disposal of the warm water, (ii) the impact of the dissolved solids on the equipment the cooling water comes in contact with, (iii) corrosive action of such water, under the conditions, on the metal of the equipment, (iv) as a consequence, the sluggishness in the 'energy exchange' system, (v) the resulting adverse impact on the production etc. etc. These and similar associated problems make the cooling waters look quite complicated and their treatment a combursome and complicated as well as expensive scientific technique which in turn adds to the entire cost of production.

The cooling waters would thus be required to be treated by a number of 'ways'. 'Inhibition' are used to 'free' the waters from the corrosive materials naturally present in the waters, or atleast to minimise their impact as best as possible. The 'inhibitors' will have their own characteristics and may behave differently; the conditions and the environment in which the inhibitors are expected to operate too will modify their behaviour. Obviously, a number of variables will be at work; a 'combined' play will be emerging out the total reactions - some quite 'matching' i.e.

'compatible', and others non-compatible. A detailed study of the relevant aspects will always be necessitated for deciding the nature and course of the treatment, keeping in mind the desired results. While a thorough study involving all the probable aspects will be out of the scope of any single dissertation, a few could always be worked out by limiting the scope and choosing the inhibitors for obtaining the desired impact.

The present study deals with five waters and five systems of inhibitors. These waters are actually from the plants of the GSFC, Baroda and the inhibitors chosen are the most recommended ones for getting the desired results.

Table 68

Inhibitors and Waters

Sr. No.	Inhibitors	Waters Plants				
1.	Benzotriazole	Ammonia	Ammonium Sulphate	Urea	Caprolactum	Makeup
2.	Corobit EPA 529	"	"	"	"	"
3.	Aquacid-105	"	"	"	"	"
4.	D A P	"	"	"	"	"
5.	Aquacid-105 + D A P	"	"	"	"	"

The waters chosen for the study were stored from the various plants as mentioned in Table 68; since once stored amount was not sufficient for the entire study as planned, the 'waters' were stored in three lots over the two years' span of the investigation. The first 'store' was studied with three inhibitors - (i) Benzotriazole, (ii) corobit EPA-529 and (iii) Aquacid-105. The second lot was utilized to study DAP and the third lot for the mixed inhibitor system of Aquacid 105 with DAP. The three 'lots' of waters stored obviously would differ in their contents and therefore all the three lots have been fully analysed and their effectivity has been considered on the basis of these three different analyses. Naturally, only a relative picture can emerge while maintaining the general trend as comparable.

(i) Benzotriazole

A glance at the analysis (Table 18) of 'Ammonia Plant' waters indicates that the water is very much alkaline with total dissolved solids 827 ppm. It can be both corrosive and scale forming. Obviously, the importance of the study of such waters is self-evident. With the presence of Cl^-, PO_4^{---}, SO_4^{--}, and NO_3^- ions, the chemical reactions with the metals this water may come in contact with, are going to be in the favour of corrosive products. This cooling water, however, even in the absence of any inhibitor, will be only mildly corrosive. The standard sample prepared as prescribed in the experimental chapter, after being immersed in the said cooling water for three days shows an insignificant corrosion rate of 1.41 mpy.

The corrosion that occurs on this sample seems to be uniformly spreading; the specimen when made ready for the experimental testing had a very bright surface, almost comparable to a 'stainless' bright surface. After three days of immersion, the brightness disappears even if the depth of the oxide film seems not to be the same throughout the surface area which gives the impression of uneven corrosion effect. However, since no 'bright' spots could be traceable, the oxide film due to corrosion must be assumed as uniformly spread even if the depth of the film may vary.

The most striking observation is that the corrosion rate for the specimen decreases to 1.14 mpy after seven days of immersion. It wouldn't be striking if it were to decrease further on longer exposure to the corrosive environment that the said cooling water provides, since a decreasing order of corrosion rate would have been taken as a normal feature in that event. However, quite contrary, the corrosion rate increases to 1.80 and 2.77 mpy for fifteen and thirty days of exposure respectively. In other words, the pattern of the change in corrosion rate is that of 'increase' first, followed by 'decrease' and then 'increase' in a continuous manner. It is this 'pattern' of 'irregular' nature that is viewed as a striking feature.

This 'irregular' pattern is not surprizing though. A simultaneous glance at the water analysis (Table 33, ammonia cooling water's column) reveals the changes in the pH values that take place. To start with the pH of the ammonia cooling water is 7.39; after three days, the pH increases to 8.26 and then falls off to 7.62 after four more days (totally seven days). It is further enhanced to 8.40 after fifteen days, but shows a slight decrease to 8.33 after 30 days. Besides other factors, the changing pH should find some correlation with the 'irregular' pattern of corrosion rate in the blank ammonia cooling water as described above.

The pH value of 7.39 for the blank ammonia cooling water initially, may be said to be slightly alkaline. The alkaline condition would induce corrosion activity under the circumstances. As seen, above, the corrosivity is only 'mild' or rather 'negligible' with the rate as 1.41 mpy during the first three days of exposure. Yet it is sufficient to yield a film over the metal surface as discerned by the disappearance of the brightness of the surface, over a period of three days; simultaneously the pH increases to 8.26. Corrosion activity is thus found to enhance pH of the medium indicating thereby the hydroxyl ions going into solution. But by the end of seven days' duration, the pH is decreased by about 0.64 reducing the corrosion rate by about 0.27 mpy. While this observation is quite reasonable in the sense that with decreasing alkalinity, corrosion rate should be decreasing in some proportions, it is striking in the sense that the alkalinity is decreased. It appears that between the 3-day and 7-day period, the hydroxyl ions do not pass into the medium. They should be adhering to the metal surface and blocking further chemical reaction leading to degradation of the metal which ultimately results into the decreased corrosion rate.

However, as more time passes, the layer of the corrosion products, seems to be loosened and passed into the medium once again. This process seems to continue unhindered days after days giving rise to enhanced corrosion rate and alkalinity. It is true that between 15 day and 30-day operation period, while corrosion rate continuously increases, the pH of the medium is nominally decreased by 0.07. It appears that, as far as these observations are concerned, the corrosion rate will continuously increase as the pH increases beyond 8.0, depending upon the days of exposure, while pH value may slightly fluctuate. Thus increase of pH value beyond 8.0 and the number of days of exposure are the two important factors working for corrosion. Besides, the other thing to make a mental note of, at this stage, is the adherence of the corrosion products to the metal surface between 3 and 7 days, which is somewhat greater than either before or after this span of time. It is this adherence power which blocks further corrosive activity; this factor seems to be the only fact or explaining the decreased corrosion rate at this moment.

While the maximum corrosion rate obtained after 30 days of exposure is only such as to be termed 'mild' the impact of the addition of the inhibitor, namely benzotriazole, may be first taken into account before discussing other aspects. In almost identical conditions of volume and temperature of the cooling waters, and the nature and size of specimens, it is observed that even small additions of the inhibitor benzotriazole do inhibit corrosion activity to a great extent; depending upon the number of days of exposure and the varying composition of the inhibitor, the corrosive activity too varies a great deal. The variations as observed are quite interesting ; the 'inhibition' pattern follows a typical path as the concentration of the inhibitor benzotriazole increases.

It can be seen from Table 33 that with 0.1% (wt/vol) addition of benzotriazole, the corrosion rate is cut down to 0.084 mpy. The difference of corrosion rates between the untreated and treated waters (ammonia cooling waters) is 1.326 mpy. This reduction in the corrosion rate amounts to about 94 % efficiency, which must be taken as quite abnormally effective one.

Table 69

% Efficiency of the Inhibitor Benzotriazole

(Ammonia cooling waters)

	% Concentration of the inhibitor (wt/vol)				
	0.1	0.2	0.5	1.0	2.0
Difference in corrosion rate mpy :'x'	1.326	1.318	1.332	1.335	1.271
%Efficiency in reducing corrosion rate	94.04	93.48	94.47	94.68	90.14

% Efficiency in reducing the corrosion rate

$$= \frac{x \times 100}{y}$$

where x = difference in the corrosion rate,

y = corrosion rate with untreated cooling waters.

A glance at Table 69 will indicate the % efficiency in reducing the corrosion rate, decreasing as the concentration of BZT (benzotriazole) increases from 0.1% to 0.2 %. It means that while the inhibiting property of BZT is well exhibited, the efficiency of inhibition is somewhat decreased. With 0.5 % concentration of the inhibitor, the efficiency is regained; now it is about 94.46 %, slightly more than that with 0.1% concentration. As the concentration is now doubled, say 1.0% the efficiency in reducing corrosion rate reaches the maximum value of 94.68 %. At 2.0 % concentration, however, the efficiency in reducing corrosion rate stemps down to just

90.14 %, which is, incidentally, the lowest for a 3-day exposure. While a generalization of either increasing or decreasing efficiency in corrosion inhibition, as the concentration of the inhibitor increases is not possible to draw, the changing efficiency has to be accounted for in terms of the chemistry of inhibition and other factors. However, before this aspect is taken up for discussion, it would be better to discuss the trends of inhibition for all the exposure periods planned under this investigation.

In the case of 7 day exposure, the overall pattern of inhibition by benzotriazole is almost the same as that for the 3-day exposure described above. It is recollected that the corrosion rate for the blank ammonia cooling waters (untreated) is otherwise also less than that for the 3-day exposure period; with the addition of the BZT inhibitor, the corrosion rate is reduced to a great extent. The reduction in corrosion rate in this case is almost twice or even more than that observed for the 3-day exposure period. This comparison can be had from Table 70.

Table 70

Comparative Reduction in Corrosion Rate 3-day & 7-day exposure period

Inhibitor : Benzotriazole

Corrosion rate: mpy	Concentration of the Inhibitor % wt/vol 0.1	0.2	0.5	1.0	2.0
Corrosion rate =3-day exposure	0.084	0.092	0.078	0.075	0.139
Corrosion rate =7-day exposure	0.031	0.030	0.039	0.043	0.063
Difference in corrosion rate	0.053	0.062	0.039	0.032	0.076

Indeed the inhibition provided for the 7-day exposure period is remarkable; this unique trend of inhibition by the benzotriazole inhibitor is continued for the subsequent 15-day and 30-day exposures. With certain exceptions, the maximum inhibition offered by the inhibitor in all the concentrations taken for the study, is for the 30-day exposure (Table 33).

However, the blank corrosion rate, as already noted earlier (Table 33) for each exposure period varies, and with the exception of the 7-day exposure period when the blank (untreated ammonia cooling water) corrosion rate is the minimum, it increases as the span of exposure increases. It is for this reason that the inhibition efficiency (in reducing the corrosion rate) for all these exposure periods and corresponding concentrations of the inhibitor, varies only proportionately. A glance at the Table 33 will reveal for 0.1 % concentration of the inhibitor the efficiency in reducing the corrosion rate becomes 97.28% for 7-day exposure, 98.27 % for 15-day exposure and 99.13 % for 30-day exposure. It can be generalized that the % efficiency increases with increasing exposure period. However, with increasing composition of the inhibitor, the efficiency changes somewhat irregularly. The inhibition efficiency is either only slightly varying (infinitesimally lesser) or almost the same for 0.2 % concentration when compared with that for 0.1 % concentration of the inhibitor. Again, though in a relative sense appreciably lesser, the picture for 0.5 % concentration is almost comparable to those of 0.1 % and 0.2 % concentrations. But with higher concentrations is of the benzotriazole inhibitor, the inhibition efficiency is decreased, it is much more decreased (on a relative scale) for 2 % concentration than that for 1 % concentration. It may be generalized that better results in terms of inhibition are obtained between 0.1 % and 0.5 % concentration; this certainly is an encouraging feature from the inhibition economics view point. Undoubtedly there are some exceptions, but that can be viewed more as experimentally accidental error, though several sets of the same experiments have yielded repeatable results.

Variations in the pH values for varying concentrations and days of exposure too are interesting; a definite pattern is discerned. Initially the pH is slightly on the alkaline side for 0.1 % and 0.2 % concentrations of the inhibitor in ammonia cooling waters. As the concentration increases to 0.5 % onwards, the pH of the water decreases from 6.71 to 6.30. With rising concentration of the inhibitor, the pH should be changing to slightly acidic side; therefore, the pattern of the initial pH with varying concentrations, with blank water being definitely alkaline, tending towards acidic range is quite natural, the inhibitor having acidic reaction.

After 3 days of exposure, the cooling waters under reference, for almost all the concentrations, turn out to be acidic as their pH values range between 5 and 6. Benzotriazole enters into specific chemical activity thereby forming almost uniform film on the metal surface, and transforms the aqueous environment, which without the addition of benzotriazole was quite alkaline, to be acidic. In the same sequence, a 7-day exposure brings about more chemical activity between benzotriazole and metal surface turning the aqueous environment still more acidic since now the pH values of the aqueous solutions for all the concentrations turn out to be lesser than those for the 3-day exposure in a corresponding manner. After 15 days of exposure of the specimen to the aqueous environment, the pH values rise and range between 6.2 and 6.9. This trend of rising pH values continues and with 30 days of exposure, the aqueous medium shows changes of pH values between 6.52 and 7.24; these values of pH are slightly higher than those obtained immediately after dissolving benzotriazole in various proportions into the ammonia cooling waters (Table 33). In short, with the addition of the inhibitor in various concentrations ranging from 0.1 % to 2.0 % and dipping the metal specimen in them, the pH values, from initially slightly alkaline in the range of about 7.0, pass through acidic values for 3 days and 7 days of exposure, acidic to somewhat neutral values for 15 days exposure and finally assume their original or slightly more alkaline range by 30 days of exposure. This path of alkaline to acidic to alkaline sojourns is definitely interesting and indicative of the chemical activity the inhibitor induces over the metal surface and within the aqueous environment.

Benzotriazole can be structurally represented as follows:

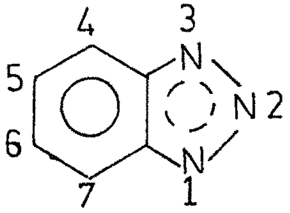


Fig. 14: Structure of benzotriazole

Its remarkable inhibitive property is linked with the molecular structure; its ligand forming capacity with copper and other transition metals and their alloys are studied (115-130) in good details. Copper is shown to give a protective film of 1:1 complex of Cu(I) and BZT (115,127,130) which is assumed to be polymeric (127). BZT is shown to bridge two copper atoms via N_1 and N_3 (Fig.14). The aromatic ring is aligned parallel to the metal surface. The film formed acts to retard cathodic reduction of oxygen although some dispute this stand and emphasize that mixed or predominantly anodic control (128) of corrosion constitute the inhibitive mechanism.

The metal specimens investigated under the current project are of specific steel as mentioned earlier. The parallel of copper may work as a guideline for the behaviour with steel. Iron is less studied with benzotriazole, however, Fe as such has the tendency of forming tetrahedral and octahedral complexes. (131). Some investigation (132) is also carried out wherein synthesis and x-ray diffraction studies of complexes of transition metals with benzotriazole are reported; in the case of iron, the report suggests $FeCl_3 \cdot 2L$ type complex formation. It would have been interesting to investigate the mechanism of complex formation for Fe with benzotriazole, however, the main object of the investigation has been to explore the applicability and the extent of efficiency of various inhibitors which did not permit the diversion despite a tempting academics having been involved.

Whatever be the mechanism, what emerges as certain is formation of a complex, mostly polymeric, in acidic range of pH. This observation under this investigation supports the view of benzotriazole assuming ionic form in aqueous solution and forming complex under changed condition. Tadashi (133) proposed the following equation for assuming an ionic form:

$$C_6H_4N_2 \cdot NH = C_6H_4N_2N^- + H^+$$

There seems to be a film formed over the metal surface; the film thicknes as the co-ordination forces continue operating.

The corrosion rate falls quickly though between 15 and 30 days of exposure the fall is more steady. An impervious film of sufficient thickness would present further corrosion since the metal surface would be fully covered. The film grows in thickness as the exposure time increases; it may also be expected to grow as the concentration of the inhibitor increases. However, the factual happenings are not that simple. The maximum impact in decreasing the corrosion rate by way of inhibition due to formation of impervious film of BZT complex with Fe, may be said to be between 0.2 % and 0.5 %, on an average. Any further addition of the inhibitor is not only useful in cutting down the corrosion rate, but it slightly increases it. In otherwords, there is a slight adverse effect at higher concentrations then 0.5 %.

However, the pH value decreases as the concentration of the inhibitor increases. This action-effect is only natural, since the H^+ ions produced due to the reaction of benzotriazole with water would be greater with higher concentration. While acidic or near acidic nature of the aqueous solution and its increasing tendency with increasing concentration is thus explained, this may be the reason for decreasing efficiency in reducing the corrosion rate. It appears that increasing quantity of H^+ ions is capable of either cracking the film at a number of places or slightly effective in partially peeling off the film or both; as a result, the efficiency of corrosion rate reduction goes down with increasing concentration of the benzotriazole inhibitor.

Surprisingly, the conductivity of the initial aqueous solution of benzotriazole in ammonia cooling waters remains the same whether the concentration is 0.1 % or 2 %. For all the concentrations from 0.1 % to 2 %, the conductivity is 1365. As a matter of fact, with increasing concentration the conductivity of the aqueous medium should have increased, since the pH values range from 7.19 to 6.30 as the concentration increases. Decreasing pH values as the concentration of benzotriazole increases is in keeping with the ionization, ih aqueous condition, of the inhibitor. It may be said that the number of ions responsible for conductivity seems not to be changing as the pH falls, which, though strange, possibility cannot be just ruled out since other factors may be playing an unusual role. This aspect may be taken up a little later when almost all waters taken for this investigation are examined in a similar manner.

A complete analysis of Ammonia cooling waters is given in (Table 18). The total dissolved solids are 827 ppm against total hardness of 280 ppm. The Cl' ppm quantity is 94; this will have some impact on the inhibition property of benzotriazole on steel. The dissolved solids may have greater relevance with reference to scaling and fouling and therefore will be taken up for due consideration at a later stage.

Ammonium sulphate cooling waters differ quite a lot from the ammonia cooling waters. These waters are more corrosive as is evident from the corrosion rates established for them under the studies carried out in this investigation. The specimens are exposed to the corrosive aqueous environment in the same manner as employed in the case of ammonia cooling waters. When the exposure time is of 3-days, the corrosion rate (Table 36) is 5.61 mpy. This corrosion rate may be viewed as moderate. For a similar exposure, the corrosion rate in the case of ammonia cooling waters is 1.41 mpy which was taken as 'mild' one. The difference in corrosion rate is of 4.20 mpy; this is indeed quite impressive difference. In Table 71 are given the difference values of corrosion rates for different exposure times. It is observed that the difference in corrosion rates is of decreasing order versus the increasing order of exposure time. It is quite pertinent to note that the corrosion rate for the blank ammonium sulphate cooling waters decrease without exception in a continuous manner as the exposure time increases from 3 days to 30 days, unlike the one exhibited by the ammonia cooling waters where the corrosion rate increased as the exposure time increased with the exception of the 7 day period. The difference

Table 71

Blank corrosion rates in mpy

Cooling waters	Exposure time in days 3	7	15	30
Ammonia	1.41	1.14	1.80	2.77
Ammonium sulphate	5.61	4.81	4.41	4.06
Difference in corrosion rate	4.20	3.67	2.61	1.29

in corrosion rates for a situation in which one rate is of increasing order and the other of decreasing order with increasing exposure time, acquire significance in a comparative sense, more so when the 'difference' in the two rates is of the decreasing order. This way of comparative evaluation of the corrosiveness of two sets of cooling waters will establish beyond doubt the corrosive impact of the ammonium sulphate cooling water which is, in a relative sense, quite high despite the fact that the rate of corrosion falls as the exposure time increases.

The initial pH of the blank ammonium sulphate cooling water is 7.23; the water does not show any alkalinity with phenolpthalin though it shows a slight methyl orange alkalinity of 24 ppm (Table 21). The water under reference is thus a little alkaline, and the corrosion phenomenon can be expected to be quite positive. As noted above, the rate on exposure to a 3 days period is 5.61 mpy. After seven days of exposure, the rate falls to 4.81. This observation suggests that the uniform film of the corrosion product is sufficiently thick and adheres quite firmly. The net result is that of reduction in corrosion rate. Yet, the observed rate is quite high, in a relative sense, as compared to that obtained for the ammonia cooling water. With 15 day exposure period, the corrosion rate further falls and assumes a minimum rate of corrosion has a decreasing sequence as the exposure time increases, as can be seen from Table 72.

Table 72

Difference in the Corrosion Rates for the Different Exposure times

	Exposure time in days						
	3		7		15		30
Corrosion Rate mpy	5.61		4.81		4.41		4.06
Difference in Corrosion Rate		0.80		0.40		0.35	

It can be easily seen that the difference values in the rate not only decrease as the exposure time increases, but it shows a tendency to assume a constant rate of corrosion at only a little more than the 30 day exposure period. In otherwords, the film of the corrosion product will not grow thick after about 31 days or so and that the steady corrosion rate would be due to a dynamic equilibrium that may come to exist. Since this is a case of moderate corrosion, the ammonium sulphate cooling waters will need treatment by an inhibitor of such nature that can reduce the corrosion rate to a comfortable range.

The pH values of blank ammonium sulphate cooling water (Table 21), though varying depending upon the exposure time, remain above the neutral line, and maintain alkaline nature of the water. The iron surface will be reacting with the alkaline water and form hydrated oxide; but in the process will release enough OH^- ions so as to keep the alkaline nature of the water intact. An interesting feature, by way of comparison, is that ammonium sulphate cooling waters, initially as well as after specific exposure times, are slightly less alkaline in terms of the pH values than those of the previously discussed ammonia cooling waters as is evident from the difference values of pH of these two waters given in Table 73. Now, in a general

Table 73

Difference in pH values

Cooling waters	Blank	pH values Exposure time in days 3	7	15	30
Ammonium Sulphate	7.23	8.17	7.41	8.01	7.55
Ammonia	7.39	8.26	7.62	8.40	8.33
Difference	0.16	0.09	0.21	0.39	0.78

sense, the corrosion is expected to be governed by the alkaline condition; the higher the alkalinity, the greater the corrosiveness of the aqueous medium. In otherwords, the ammonia waters should have been as much corrosive, if not more, as the ammonium sulphate waters, for the same steel specimens are studied in both waters. However, this particular point may be taken up for discussion after all waters studied under this investigation have been accorded for in terms of their corrosiveness, not only because this aspect is rather emerging as common but also because the composition of all the waters seen at a glance do not seem to offer explanation for this behaviourism.

Benzotriazole is added to ammonium sulphate cooling water in different amounts to investigate its inhibiting characteristics. The compositions are 0.1, 0.2, 0.5, 1.0 and 2.0 % (weight/volume). It is observed that (Table 36) with 0.1 % composition of the inhibitor; the corrosion rate slumps down to 2.00 mpy for a 3-day exposure time, the blank corrosion rate being 5.61 mpy. This means that the corrosion rate is reduced by 3.61 mpy. The corrosion rate is further reduced to 1.88 mpy with 0.2 % concentration of the inhibitor benzotriazole. However, thereafter, with increasing concentration of the inhibitor, the corrosion rate, though much less than that of the blank water, increases as one proceeds from 0.5 % to 2.0 %. For a 3-day exposure time, 0.2 % concentration of benzotriazole yields the best result with the corrosion rate being just 1.86 mpy. From moderately corrosive water, it becomes just mildly corrosive with additions of benzotriazole in small amounts which speaks for the inhibiting capacity of the inhibitor. While for a 3-day exposure time, the minimum corrosion rate, and hence the maximum inhibition efficiency, is given by 0.2 % concentration of benzotriazole, for 7-day exposure time it is given by 0.5 % concentration and for 15 day and 30 day exposure times 1 % concentration of the inhibitor. It can be generalized that just as the exposure time increases, the % concentration that can assume maximum inhibition efficiency, also increases, but the ultimate quantity required is not more than 1.0 % (Table 36).

The inhibition efficiency (Table 36) is maximum for a 15-day exposure time, on an average, though it varies differently depending upon the exposure time and % concentration of benzotriazole. However, as discerned from Table 36, the maximum inhibition efficiency with lower concentrations, say 0.1 % and 0.2 % is for 3-day 7-day and 15 day exposure times and with higher concentrations, say 1.0 % and 2.0 % of benzotriazole, is for 30 day exposure time. This leads to believing that if the exposure time is 15 days and more, then to obtain maximum efficiency in corrosion inhibition, higher concentrations of the inhibitor to be employed, with medium concentration of about 0.5 %, the efficiency of inhibition increases on an average with increasing exposure time. Another point of interest that emerges is that except for 0.5 % concentration of benzotriazole the % inhibition efficiency alternates with 3, 7, 15 and 30 days of exposure time.

It should be noted that the % inhibition efficiency for the same concentration of benzotriazole is greater in the case of ammonia cooling waters than of ammonium sulphate cooling waters for the corresponding periods of exposure time.

Table 74

Comparative Efficiency

Cooling waters	% of Benzotriazole 0.1	 0.2	 0.5	 1.0	 2.0
	3 day exposure time				
Ammonia	94.04	93.48	94.47	94.68	90.14
Ammonium sulphate	64.35	66.49	64.71	58.82	63.64
Difference	29.69	26.99	29.76	35.86	26.50
	7 day exposure time				
Ammonia	97.28	97.37	96.58	96.23	94.47
Ammonium sulphate	50.10	62.58	64.45	58.21	62.16
Difference	47.18	34.79	32.13	38.02	32.31

In Table 74 are given the difference values of % inhibition efficiency of two cooling waters viz ammonia and ammonium sulphate, for the various concentrations of benzotriazole, for 3-day and 7-day exposure times. The difference values clearly indicate the overwhelming efficiency of benzotriazole for ammonia cooling waters. Almost the same efficiency trend is discerned for the 15-day and 30-day exposure times.

The initial pH values for the various concentrations of benzotriazole in ammonium sulphate cooling waters, by and large, remain within the acidic range. For higher concentrations of about 1 % and 2 %, the pH range is definitely acidic, which is less than 6.0 or only slightly above by + 0.1 barring a few exceptions. For lower concentrations it ranges from slightly acidic to neutral to slightly basic. It is thus only reasonable to view the aqueous environment where benzotriazole is by and large present as molecules; its slight ionization relative to pH cannot be taken as predominant. But on exposure versus time and with slightly higher concentration, at a stage when sufficient chemical activity has been brought into play for forming a non-pervious film due to complex formation, the aqueous environment is sufficiently acidic which will indicate passing of H^+ into the solution after the complex formation has taken place releasing H^+ ions. However, for 15 day and

30 day exposure times with 0.1 % and 0.2 % benzotriazole, the pH values are either in slightly alkaline range or are neutral on the verge of alkalinity, the corrosion rate is sufficiently higher than the expected value of the reduced rate. Thus, the role of pH becomes clear as far as the effectivity of benzotriazole as inhibitor is concerned.

Again, the conductivity measurements of the solutions of benzotriazole ranging between 0.1 % and 2.0 % in ammonium sulphate cooling waters, indicate the molecular state of benzotriazole in solutions, since the value (conductivity) remains the same (964 micromhos) for all the concentrations. Since, the conductivity of the aqueous medium after exposures for definite intervals of time has not been ascertained, a definite view regarding the molecular state or ionised condition if benzotriazole may not emerge, and yet, from the pH values after the exposure periods, speaks for the increase of H^+ ion concentration. Therefore, it may fairly be concluded that as soon as complex formation is initiated with benzotriazole, the loosely attached H simultaneously detaches, making the moiety ionised. Hence, it is reasonable to assume the complexing reaction to be proceeding between the steel surface and ionised benzotriazole moiety.

The urea cooling waters are more corrosive than either ammonia or ammonium sulphate cooling waters, as is seen by the blank corrosion rates for all the four exposure times

(Table 35). However, unlike that of ammonia cooling waters and in keeping with the ammonium sulphate cooling waters, the urea cooling waters present a decreasing rate of corrosion as the exposure time increases. This fact can be better realized by comparing the difference in the corresponding rates of corrosion.

Table 75

Difference in Corrosion rates

	Exposure time in days						
	3		7		15		30
Corrosion rate mpy	6.56		4.89		5.35		4.04
Difference in corrosion rate mpy		1.67		0.46		1.31	

The difference in the corrosion rates derived in Table 75 may be compared with those derived in Table 72. At a glance it can be seen that the difference values in corrosion rates in Table 75 are greater than the corresponding values given in Table 72, indicating thereby that the blank rates of corrosion for urea cooling waters are much higher. As a matter of fact, as it will finally emerge, the urea cooling waters of the GSFC Baroda are most corrosive of the four plant waters undertaken for the study.

It may further be pointed out that, while the corrosion rates of the blank urea cooling waters decrease in a general way as pointed out above, the 15-day exposure corrosion rate is higher than that of the 7-day exposure as well as of the 30 day exposure corrosion rates. This pattern of decreasing rate turns out to be alternately higher and lower, and differ from the continuous decreasing pattern of the ammonium sulphate cooling waters. It is for this reason that the difference value shown in the third column of Table 75 is with negative sign.

The pH values of blank urea cooling waters (Table 35) for various exposures time are in quite alkaline range which is an indication of corrosive environment, that these values are by and large higher than those for both previous cooling waters (Table 33, 36) is evidence enough for higher corrosive tendency.

Addition of benzotriazole has good inhibitive effect in the case this cooling water. In this case again the corrosion rate (Table 35) decreases as the % concentration of benzotriazole increases. Obviously thus, in contrast to the observations in the case of previous both cooling waters, it is discerned that the greater the amount of benzotriazole the higher is efficiency in reducing the corrosion rate. Apart from the 'alternating' effect in the corrosion rates, while maintaining a decreasing tendency in corrosion rates, the exposure time has its own impact on the corrosiveness of the waters in question. It can be said that the higher the exposure time, the greater is the efficiency in reducing the corrosion rate. It is also of interest to note that the alternate pattern of less and more reduction in corrosion rate as the exposure time increases, in a similar manner as for the blank waters observed and described earlier, is well maintained for 0.1 % and 0.2 % concentration of benzotriazole. For higher concentrations of 0.5 %, 1.0 % and 2.0 % the corrosion rates are not only reduced in a continuous manner as the concentration increases, but are also continuously reduced in a corresponding manner as the exposure time is increased. In other words the higher concentration and the greater exposure time being about the maximum efficiency in cutting down the corrosion rate. The two factors work in remision. It further means that with about 2 % of benzotriazole will work effectively once the steel is exposed for about 30 days in giving high protection to it by way of inhibition.

It can be seen from Table 76 that the inhibition efficiency with 2.0 % concentration of benzotriazole inhibitor as displayed is greater in the case of urea plant cooling waters than that displayed by ammonium sulphate plant cooling waters in a corresponding manner of exposure time.

Table 76

Comparison for 2.0 % benzotriazole Efficiency in reducing Corrosion Rates of Ammonium Sulphate cooling waters and Urea cooling waters

Cooling waters	2.0 % concentration % Inhibition efficiency			
	Exposure time			
	3	7	15	30
Ammonium sulphate plant	63.64	62.16	72.34	84.98
Urea plant	73.32	73.82	87.66	86.88
Difference in inhibition efficiency	9.68	11.66	15.32	1.90

A glance at the pH variations with increasing concentration of benzotriazole and exposure time would provide the reasons for the inhibition efficiency being greater at higher % concentration of the inhibitor. The pH values for aqueous solutions of 1.0 % and 2.0 % concentrations for almost all exposure times except one, fall within the acidic range - a condition which is conducive to decreased corrosion. For the concentrations 0.1 % and 0.2 % of the inhibitor, the pH values of the aqueous solutions for almost all exposure times except one happen to be in the alkaline range, a condition conducive to corrosion. However, since a non-pervious film of the metal-inhibitor complex is formed, the corrosion rate is cut down, but the inhibition efficiency does not approach that exhibited by the higher concentrations of the inhibitor. Almost similar is the case of 0.5 % concentration. The requirement of higher concentration of the inhibitor to render the aqueous environment well within the acidic range seems to be the cause of lesser inhibition efficiency with lower concentration of the inhibitor. It also means that besides formation of a continuous and impervious metal complex film by benzotriazole, which is the main mechanism of providing protection against corrosion in the corrosive aqueous environment, larger amount of H^+ ions released by the inhibitor on account of complexing activity with the metal surface helps cutting down the corrosion rate further and enhancing the value of the inhibiting material as an inhibitor. As is discerned from these observations, in absence of the latter process, the film formation may be quite in tune for affording protection, but the inhibition efficiency may be proportionately impaired.

The total dissolved solids and other characteristics as noted in (Table 18-22) do not seem to be related contributing to the corrosiveness of the cooling waters and hence their role in inhibition activity seems to be unrelated. The urea plant cooling waters, blank as well as containing dissolved amount in varying proportions of benzotriazole, have been subjected to conductivity measurement. For all concentrations inclusive 0.0 %, the conductivity is 2248 micromhos. Unchanging conductivity indicates that benzotriazole is in molecular condition when dissolved in urea plant cooling water. This again supports the view as evolved earlier that H^+ ions are released into the aqueous environment by the inhibitor only after the complexing activity begins. These observations go in support of the earlier contention of some research workers that benzotriazole in solution in water can give rise to form molecular to ionized state.

The caprolactum plant cooling waters are also corrosive; these cooling waters are more corrosive than the cooling waters of ammonia plant but less than those of ammonium sulphate plant and urea plant (Tables 33, 34, 35, 36). But the initial pH of caprolactum plant cooling waters is 8.07 which is more than that of any of the three cooling waters discussed so far. On the basis of this criterion of alkalinity alone, the caprolactum plant cooling waters should be most corrosive of the cooling waters taken for consideration so far. However, the observed fact is quite contrary and demands explanation. This aspect though may be given consideration a little later.

The rate of corrosion for blank caprolactum cooling waters, for all the four exposure times of 3, 7, 15 and 30 days, decreases as the exposure time increases with one exception that is for 7-day exposure where it is higher than the preceding lower or succeeding higher exposure times. In Table 77 are given the difference values for the exposure times which show the difference values in the decreasing order as the exposure times increase with the exception of 7-day period where the corrosion rate increases by 0.58. Regarding this typical behaviour, the explanation can be found in the changing pH values of the cooling waters for different exposure times. The pH values (Table 34) for the blank caprolactum plant cooling waters decrease from the initial 8.07 successively against the exposure times, to 7.09 for 30 day period except for the 3-day period when it increases to 8.36.

Table 77

Blank Corrosion Rates in mpy

	Exposure time in days						
	3		7		15		30
Corrosion rate mpy	3.61		4.19		3.06		2.76
Difference values		+0.58		1.13		0.30	

In otherwards, the decrease in corrosion rates as the exposure time increases, inclusive of the 3-day period when the corrosion rate increases, can be linked with the similar pattern of changing pH values.

The decreasing corrosion rate is on account of formation of hydrated oxide film on the metal surface. This film grows in thickness and then would work as a cover for further exposure to chemical attack. Thus the corrosion rate will dwindle. However, it does not tend to be zero perhaps on account of some of the hydroxide corrosion products being soluble as a result of which some chemical activity will be continued. This results into two things (i) maintenance of the corrosion rate, though greatly reduced and (ii) maintaining the pH of the aqueous medium in the alkaline range.

Benzotriazole is added to the caprolactum cooling waters in percentages of 0.1, 0.2, 0.5 and 1.0 and 2.0. The steel specimens are exposed to different periods of time, say 3, 7, 15 and 30 days. The corrosion rate for a 3-day period of exposure is reduced from 3.61 mpy for the blank to 2.53 mpy for 0.1 % concentration of benzotriazole. The corrosion rate decreases in a regular manner as the % composition of benzotriazole increases. As a matter of fact the corrosion rate decreases just as the % concentration increases as well as the exposure time increases. Thus it is both a horizontal and vertical (Table 34) pattern of decreasing corrosion rate as concentration and exposure time increase. In this particular case the % inhibition efficiency for the different concentrations and exposure times are given in Table 34; it can be easily seen that with 0.1 % concentration of the inhibitor for a 3-day exposure time, the inhibition efficiency is 29.92 %. This inhibition efficiency increases to 77.90 % with 2.0 % concentration and 30-day exposure time with 3-day exposure time and 2.0 % concentration of the inhibitor, the inhibition efficiency increases to 62.88 %. Thus while from 0.1 % to 2.0 % concentration increase, the inhibition efficiency increase is of 32.96 %; now with the same % of concentration, if the exposure time is increased to 30 days, the further increase in % efficiency is just 15.02 %. While this picture is interesting, the % inhibition efficiency with 0.1 % concentration of the inhibitor, for a 30 day exposure time is just 11.59 %. Thus, while the corrosion rate decreases as the exposure time increases, the % inhibition efficiency decreases from 29.92 for a 3-day period to just 11.59 for a 30-day time. The difference (in the direction of decreasing efficiency) in the % inhibition efficiency is 18.33; this is quite a difference as far as 0.1 % concentration unit is concerned. Versus this result, for the higher concentration, say 2.0 %, of the inhibitor, the inhibition efficiency is rather increased by 15.02 % from the original 3-day exposure time, to 30-day exposure time. In otherwords, there can be two generalizations in this case (i) for lower concentrations, the corrosion rate decreases as the exposure time increases in a manner that turns out to be one of decreasing inhibition efficiency, and

(ii) for higher concentration, the corrosion rate decreases as the exposure time increases in a manner as to enhance the % inhibition efficiency also.

The case of pH variations for the caprolactum cooling waters is also quite interesting. For lower concentrations of the inhibitor benzotriazole, say 0.1 % and 0.2 %, for all exposure times, the pH values are in either near alkaline or alkaline range; this observation is also equally true for 0.5 % concentration, but with a slight difference. However, for higher concentrations say 1.0 % and 2.0 %, the pH values fall well within the acidic range. Two points of interest emerge from these observations (i) the higher concentration is effective because a proper film of the polymer complex on the metal surface with benzotriazole in that even can be produced, and (ii) in the process, more H^+ ions are thrown in the aqueous medium, making the aqueous environment quite acidic. In otherwords, it can be reasonably said that greater protection is afforded by benzotriazole if the chemical activity is such that the aqueous environment is rendered acidic. It should, however, be noted at this stage that the initial conductivity of the aqueous solutions of benzotriazole for all concentrations, is rather the same, say 1445 micromhos. This indicates, the same way as in almost all the previous cooling waters, that the benzotriazole stays molecular in solution and turns ionic when the chemical activity with the metal surface by way of formation of a polymer complex, has taken place.

The last cooling waters in the series are the makeup waters. All the five cooling waters have been collected from the GSFC, Baroda, for this specific study. The makeup water is drawn from the adjoining river and used for making up the loss in the cooling waters which are under recirculation for the various plants. The impact of the make-up water thus will be on all the cooling waters; therefore a similar study in regard to the make-up waters became inevitable.

The blank make-up waters show 'moderate' to 'mild' corrosion rates for different exposure times, with increasing time of exposure the corrosion rate decreases. The difference values in the decreasing corrosion rates are given in Table 78.

Table 78

Difference values in Corrosion Rates

Corrosion rates in mpy

	Exposure time in days						
	3		7		15		30
Difference values	5.40		4.04		3.46		3.75
		1.36		0.58		+0.29	

It is seen from the Table 78 that the difference values in the rates of corrosion decrease as the exposure time increases, which is an indication of reaching a definite rate of corrosion which will be there without being diminished any further, though there is a slight increase in the corrosion rate towards the highest exposure time in this case. The pH values for the blank make-up waters for all the four exposure periods are in the alkaline range. Rather, the pH values increase as the exposure time increases; this is a sure indication of more OH^- ions going into solution as the exposure time increases.

The corrosion rates in the case of make-up waters decrease, with a few exceptions, as the concentration of benzotriazole as well as the exposure time increases. With 1.0 % and 2.0 % of benzotriazole, the corrosion is almost negligible; the corrosion rates with these concentrations are the lowest among all the five cooling waters and for all the four exposure times. The % inhibition efficiency from 53.89 with 0.1 % concentration, for a 3 day exposure, increases to 87.78 % with 2.0 % concentration of the inhibitor for the same exposure time and to 97.07 for a 30-day exposure time. The increase in % inhibition efficiency to 97.07 is tremendous as compared to the 20.27 % efficiency with 0.1 % concentration for a 30 day exposure time. In general the inhibition efficiency in majority of cooling water was found greater with 2 % benzotriazole as shown in fig.16 and similarly with increase in exposure days inhibition efficiency increases with 2 % benzotriazole except urea plant as shown in fig. 15.

For concentrations from 0.1 % to 0.5 %, the pH values are in the alkaline range; however, with higher concentrations of 1.0 % and 2.0 % of the benzotriazole inhibitor, the aqueous solutions for almost all the exposure times, give pH values that may be said to be either acidic or nearing neutral range. Where the corrosion rates are the lowest, the pH range is found to be definitely acidic. The conductivity of the make-up water for all the concentrations of benzotriazole is the same i.e. 458 micromhos.

Except the make-up water, all other cooling waters of the four chemical plants at the GSFC, Baroda are normally pretreated and then recirculated. Their corrosive characteristics are thus pre-monitored; there will also be modulations depending upon the variations in the pretreatment. Therefore, the cooling waters from the different plants were stored in sufficient quantities so as to maintain the same characteristics for studying the impact of the inhibitor benzotriazole.

It is because of this pretreatment aspect that the blank corrosion rates of these waters differ, though the location of the company would indicate the same source from where the first stock of cooling waters was stored. From a sketchly information about the pretreatment, it is observed that ammonia plant cooling waters and caprolactum plant cooling waters have been, besides other treatments, treated with polyacryloamide which may be the reason why these two waters are least corrosive. Here too, the amount of this material used in ammonia plant cooling waters in ten times of that used in caprolactum cooling waters; thus the ammonia plant cooling waters are only negligibly corrosive.

Against this background, benzotriazole as an inhibitor can be said to be quite effective in a number of cases. The 'no-change' in conductivity for all concentrations of the inhibitor in all the cooling waters selected for the study clearly indicate that benzotriazole remains in molecular condition when dissolved in the cooling waters and not in the ionized state. However, when the chemical activity takes place between the metal surface and benzotriazole in a manner as already discussed earlier, there is release of H^+ ions in the solution, and as they accumulate, the pH of the medium tends to be in the acidic range. With increasing concentrations of the inhibitor, not only the accumulation of H^+ ions in the cooling waters is greater, but the inhibition activity, in most cases, is greater since the film of metal complexes with the inhibitor benzotriazole grows in thickness as well as becomes thick enough to resist the stress and strain due to water despite the fact that the study is in stagnant condition. The corrosion rates thus dwindle.

The other analytical data of the cooling waters do not seem to be effective in modulating the inhibition characteristics of benzotriazole. A comparative evaluation of the inhibition efficiency in reducing corrosion in terms of the concentration of the inhibitor and exposure times is given in Table 79.

Table 79

Comparative Evaluation

Inhibition Efficiency

Cooling waters	Maximum Inhibition Efficiency % concentration (%) of inhibitor Exposure times in days			
	3	7	15	30
Ammonia plant	1.0 %	0.2 %	2.0 %	2.0 %
Ammonium sulphate plant	0.5 %	0.5 %	1.0 %	1.0 %
Urea plant	1.0 %	2.0 %	2.0 %	2.0 %
Caprolactum plant	2.0 %	2.0 %	2.0 %	2.0 %
Make-up	2.0 %	2.0 %	2.0 %	2.0 %

In an overall manner, a 2.0 % concentration of benzotriazole seems to be very effective though in specific cases even lesser concentrations can be workable. Certain generalizations can be arrived with the least probability of deviations.

(i) The % inhibition efficiency of benzotriazole for the steel specimen increases with increasing concentrations whatever be the exposure times.

(ii) The complex film formation activity brings about release of H^+ ions from the benzotriazole moiety resulting into variations in the pH values of the cooling waters whose blank pH values were adjusted to be around 7.0.

(iii) Since the protection afforded is plausible, the complex film formed should be quite thick and smooth and even without pores because such films can be more effective in cutting down the corrosion rates to the extent they do.

(iv) Benzotriazole with 0.1 % concentration can serve the purpose of tunning the ammonia plant cooling waters least corrosive, with 0.5 % concentration for ammonium sulphate cooling waters and about 2.0 % concentration for the other three cooling waters.

(v) More than 2.0 % concentration may never be required to achieve the maximum inhibition efficiency of benzotriazole for these cooling waters.

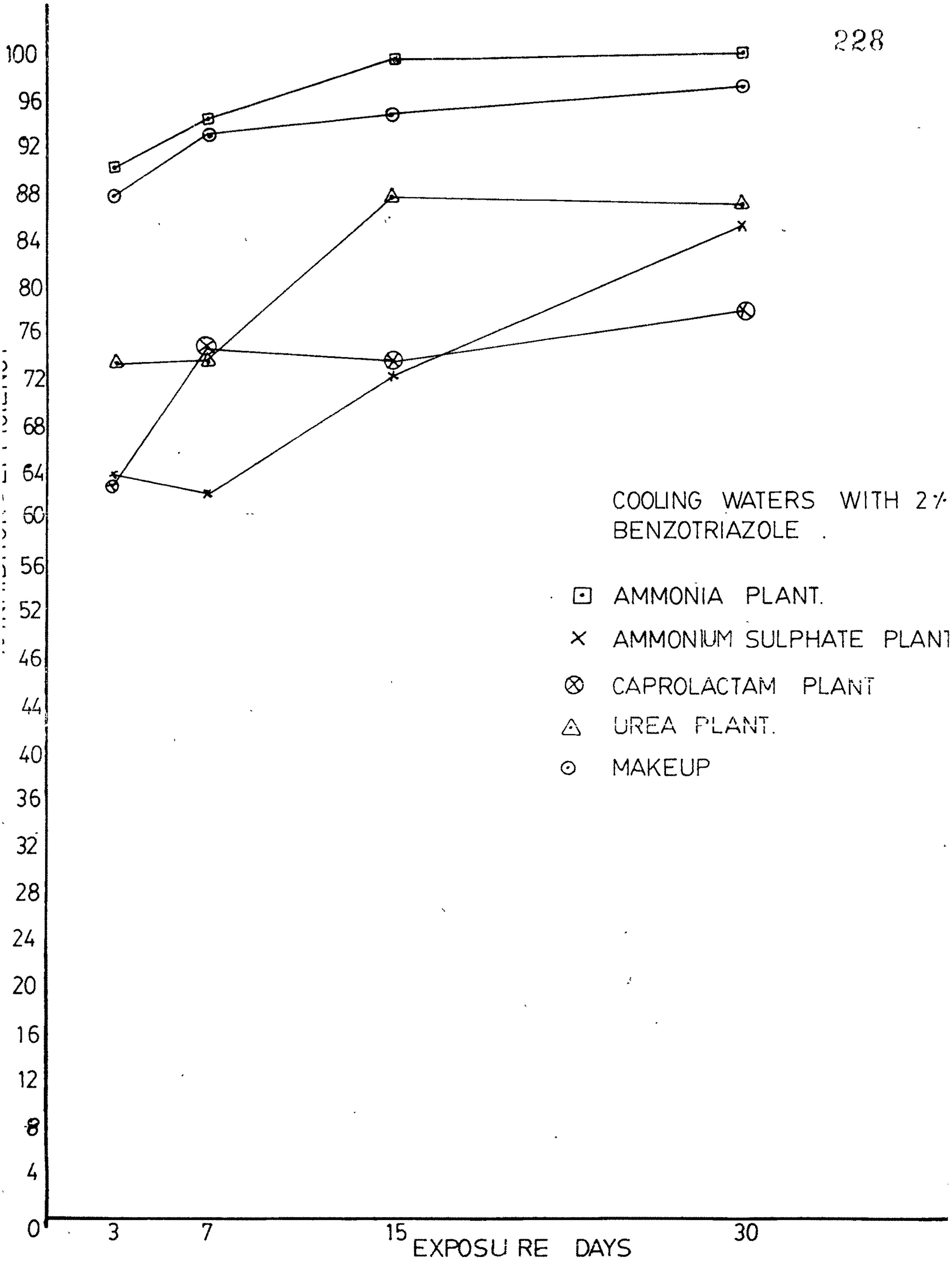


FIG. 15 COOLING WATERS WITH 2% BENZOTRIAZOLE

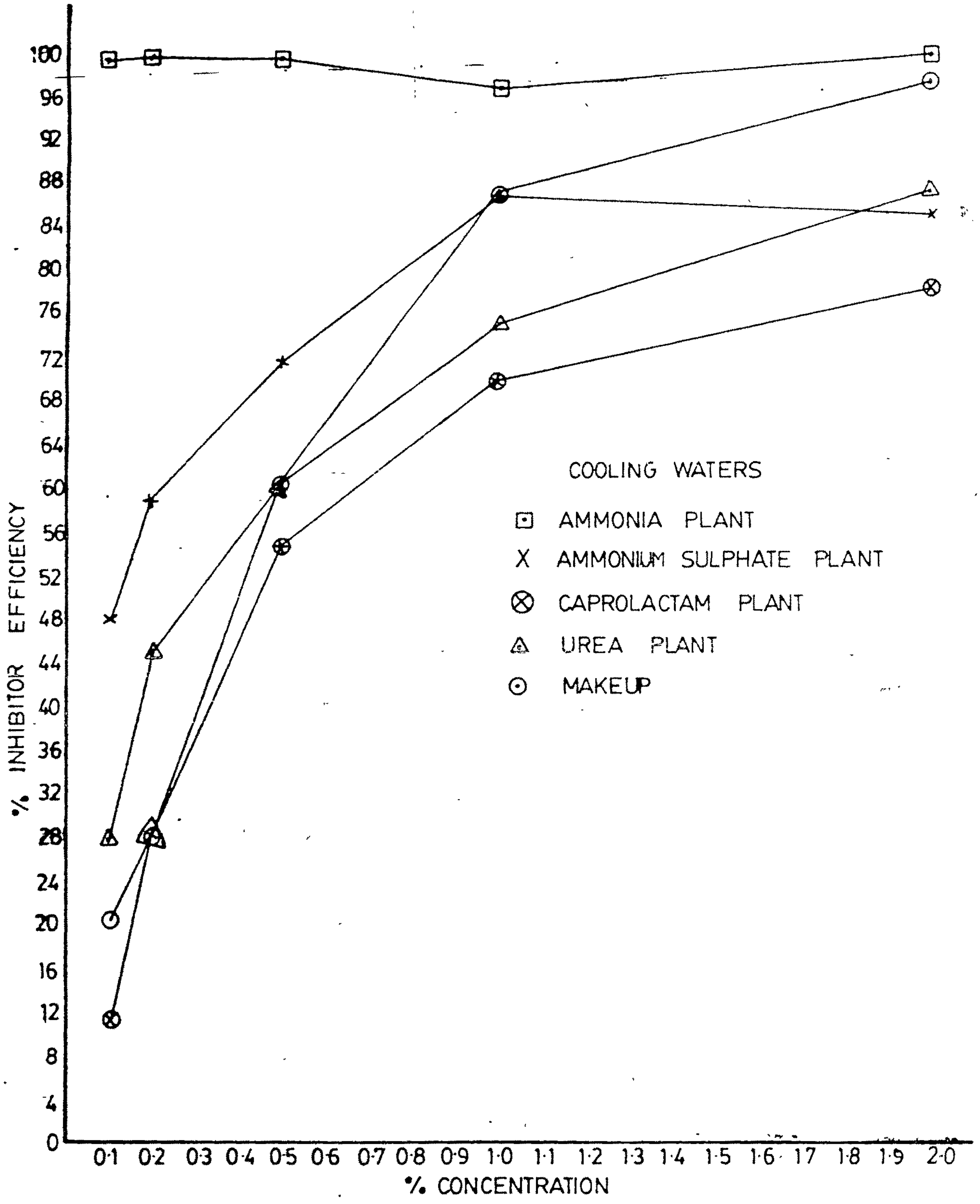


FIG. 16 BENZOTRIAZOLE-30 DAYS EXPOSURE.

(ii) Corobit EPA-529

The second inhibitor selected for the study was corobit-EPA-529; it is investigated for all the five cooling waters, four exposure times and in six different concentrations. The blank corrosion rates for all exposure times and for all the five cooling waters are the same as found while describing the results of the benzotriazole experimentation. The metal specimens also are of the same steel and specifications. Thus, the direct comparison with the previous results becomes easy.

In the case of ammonia cooling waters, as the inhibitor corobit-EPA-529 is added, the corrosive activity decreases. However, the pattern of decrease of the corrosion rates with increasing concentration of the corobit inhibitor, is rather strange. With 0.1 % (v/v) addition of corobit inhibitor, the effect is rather uncertain for a 3 day exposure period; 0.2 % addition decreases the corrosion rate by about 1.327 mpy from the blank value of 1.41 mpy (Table 38). However, with 0.5 % concentration of corobit EPA-529, the corrosion is slightly enhanced (0.088 mpy) as compared to that of 0.2 % concentration (0.084 mpy), though it is less than that of the blank value (1.41 mpy). For the next concentration of 1.0 %, the corrosion rate is further decreased (0.07 mpy). In otherwords, the corrosion rate, upto 1.0 % concentration, alternates in an overall decreasing sequence. But thereafter, as the concentration of corobit-EPA-529 inhibitor increases, the corrosion rate increased, though it is always less than that for the blank ammonia cooling waters (Table 38).

For a 7-day exposure period, the corrosion rate decrease (Table 38) as the concentration of the corobit inhibitor increases; however, it alternates for 0.1 %, 0.2 % and 0.5 % concentrations. From 0.5 % to 5.0 % concentrations, the corrosion rates increase in a sequence, though in an overall manner, they are less than that for the blank cooling water. For the 15-day period, the corrosion rate decreases as concentration increases but upto 0.5 % concentration the rate decreases in a sequence and thereafter upto 5.0 % concentration the corrosion rate increases though the rates are lesser than that for the blank water. In the case of 30 day exposure time, the corrosion rate decreases up to the 2.0 % concentration stage, but in an alternate manner. However, with 5.0 % concentration of corobit EPA-529 inhibitor, the corrosion rate increases; it is in fact more than that for the blank water by about 0.9 mpy.

Another quite interesting sequence that can be discerned is that with 1.0 %, 2.0 % and 5.0 % concentrations of the corobit inhibitor, i.e. with higher concentrations, the corrosion rates, though as such lesser than the respective blank corrosion rates, increase as the exposure time increases from a 3-day to 30-day period, with some exceptions (Table 38). On the other hand, for lower concentrations of 0.1 %, 0.2% and 0.5 %, the rates decrease, unlike the effect discerned for the higher concentrations, as the exposure time increases, albeit in this case too with some exceptions. The difference values of the increasing and decreasing pattern of corrosion rates, of course within overall decreased rates, with regard to increasing concentrations of the inhibitor and exposure times, are given in Table 80.

Table 80

Difference Values : Increasing & Decreasing Pattern of Corrosion Rates in mpy.

Exposure time in days	Concentration in % (v/v) of Corobit-EPA-529					
	decreasing				increasing	
	0.1	0.2	0.5	1.0	2.0	5.0
3	1.41	0.084	0.088	0.070	0.405	0.676
7	0.024	0.022	0.037	0.073	0.401	1,120
Diff	1.386	0.062	0.051	0.003	- 0.004	0.444
7	0.024	0.022	0.037	0.073	0.401	1.120
15	0.034	0.019	0.017	0.276	0.708	2.390
Diff	+0.010	0.003	0.020	0.203	0.307	1.270
15	0.034	0.019	0.017	0.276	0.708	2.390
30	0.063	0.010	0.023	0.011	0.715	3.670
Diff	+0.029	0.009	+0.006	-0.265	0.007	1.280

+ exceptions - exceptions

The corrosion rates for 0.1 %, concentration of the corobit inhibitor for the different exposure times is indicating an increasing pattern alongwith those for the higher concentrations. But, since a 3-day exposure fails to evolve a corrosion rate, this conclusion gets little tarnishing impact, and hence it could not be treated separately.

The Table giving the % inhibition efficiency can throw better light (Table 38) on the effectivity of the inhibitor. The % inhibition efficiency is the lowest for a 5 % concentration of the inhibitor. As a matter of fact, the higher concentration of the inhibitor give bad results which from the general economics of the plant view point is an encouraging feature. The lower concentrations work well against all exposure times. The higher the concentration and the longer the exposure, the poorer is the inhibition afforded by the corobit EPA-529 inhibitor to the ammonia plant cooling water system.

The pH values of the solutions of the corobit EPA-529 inhibitor in ammonia cooling waters for its different concentrations increase as the concentration increases. Versus exposure times, either the values are quite near each other in the alkaline range or only slightly increase for every concentration. With a 3-day exposure for a 5.0 % solution of corobit inhibitor the pH value from 7.81 for 1.0 % concentration increases to 9.64. This pattern is almost observed by all the other three exposure periods. The corrosion rates are the highest in the decreased range or even higher than the blank rate for a 5 % concentration of corobit. It is thus possible to link the increased alkalinity with increased corrosion rate and decreased inhibition efficiency. Obviously, the higher the alkalinity the higher will be the corrosion rate though decreased sufficiently as compared to the blank rate and hence the lesser the inhibition efficiency. It is the high alkalinity that accelerates the corrosion rate of the 5.0 % concentaration of corobit inhibitor for 15-day and 30-day exposure times.

As already discussed earlier, the ammonium sulphate plant cooling waters are quite corrosive, despite their pre- treatment to minimise the corrosive tendency. The inhibition accorded to this cooling water system by adding corobit-EPA-529 inhibitor is somewhat strange. The first addition of 0.1 % brings down the corrosion rate wonderfully well, for all the exposure times. In Table 81 are given the difference values of the corrosion rates which speak by themselves. It is observed that the difference values show a pattern of near constancy with an average of about 3.70. While the decreased corrosion rates, which are in the decreasing order as the exposure time increases, differ, the blank corrosion rates too differ in almost a proportionate manner, with decreasing sequence; hence a near

Table 81

Difference caused in the Corrosion Rates

Corrosion Rate mpy	Exposure time in days 3	7	15	30
Blank	5.61	4.81	4.41	4.06
0.1% concentration of the corobit Inhibitor	1.66	1.18	0.81	0.45
Difference	3.95	3.63	3.60	3.61

'constant' difference value pattern is obtained. However, the % inhibition efficiency will differ on account of the blank corrosion rates (Table 41). It can be easily seen that the % efficiency is in the increasing order (Table 41) as the exposure time increases. It may also be noted that the difference values in the % inhibition efficiency for 3-day and 7-day, 7-day and 15 day, and 15-day and 30-day exposure periods are 5.06, 6.16 and 7.29 respectively, which is in the increasing order. This indicates that the relative % efficiency too increases somewhat as the exposure times are prolonged. This in turn, however indirect, indicates that the film which is adsorbed on the metal surface due to the chemical activity between it and the corobit inhibitor, gets thicker and more even as the time passes.

With higher concentrations, say 0.2 % and 0.5 % the corrosion rates, though sufficiently decreased, are in the rising order for all the exposure times. If the effect due to 0.1 % concentration is also included in this discussion, then it can be said that, though as such the corrosion rates are sufficiently reduced as compared to those for the blank waters, for all exposure times, the corrosion rates increase as the concentration of the corobit inhibitor increases. The corrosion rates for the 1.0 % concentration for all exposure times (Table 41) are again reduced sufficiently as compared to those of the preceding concentrations. But, if the corrosion rates for the higher concentrations of 1.0 %, 2.0% and 5.0 % are taken in a sequence, then the order is of increasing corrosion for some and decreasing corrosion for the other exposure times as the concentration of the corobit inhibitor increases. To find a definite trend is thus difficult, yet what can safely be said is that the inhibition efficiency is, in an overall manner, the best with the least concentration (0.1 %) and the worst with the medium concentration (0.5 %).

Now, taking into consideration the pH values of the ammonium sulphate cooling waters having different concentrations of the corobit inhibitor for all the four exposure times and the fresh waters, an interesting correlationship seems to be emerging. A close examination of the Table 41, will reveal three important pH values : (i) pH value approximately 8.0 when the inhibition accorded by the corobit inhibitor is the best on an average, (ii) approximately 8.5 pH when the inhibition is the least and (iii) pH value around 10.0 when once again the inhibition is better, say of medium efficiency range. The nature of the ammonium sulphate plant cooling waters seems to be such that the concentration of OH^- ions play a role in the formation and maintenance of the protective film on the metal surface. Since the corobit EPA-529 inhibitor is not a single compound, the chemical reactions will have to be taken into account in terms of the probable ions that may be in abundance in a given situation.

The urea plant cooling waters are the most corrosive of the lot since their blank corrosion against all the four exposure times is the highest. The impact of the corobit-EPA-529 inhibitor with 0.1 % concentration, however, seems to be somewhat better than that experienced in the previous case, as is evident from the Table 82. With the exception for the 30-day exposure where the corrosion rate is higher in the case of urea plant cooling waters, the corrosion rates are relatively lower than those for the ammonium sulphate plant cooling waters.

Table 82

Comparison of Corrosion Rates (0.1 % concentration of Corobit EPA-529) Urea Plant Cooling Waters

Corrosion Rates : mpy	Exposure time in days 3	7	15	30
Ammonium sulphate plant cooling waters	1.66	1.18	0.81	0.45
Urea plant cooling waters	1.41	0.92	0.74	0.59
Difference values	0.25	0.26	0.07	+0.14

It is of interest to note the difference in the reduction of corrosion rates as compared to those for the blank waters for all the exposure times.

Table 83

Reduction in Corrosion Rates

Corrosion rate in mpy	Exposure time in days 3	7	15	30
Blank waters	6.56	4.89	5.35	4.04
Waters with 0.1 % concentration	1.41	0.92	0.74	0.59
Difference value	5.15	3.97	4.61	3.45

Unlike the pattern obtained in the case of ammonium sulphate cooling waters, the pattern here is the one of alternate average difference values. The corrosion rates are in the decreasing order as the exposure times increases, but the difference values of the relative rates show an alternate decreasing and increasing tendency, though the overall pattern is one of continuous reduction in corrosion rates as the exposure time increases.

The corrosion rates for all concentrations and exposure times are in the decreasing order as the concentration is increased. However, the lowest corrosion rates are for the 0.1 % concentration of the corobit EPA-529 inhibitor for all exposure times with minor exceptions. This is in common with the observation for the ammonium sulphate plant cooling waters.

As such the corrosion rates are greatly reduced. However, the reduced corrosion rates are in the increasing order as the concentration increases upto 0.5 % for the 3-day and 7-day exposure times and upto 1.0 % for 15-day exposure time and upto 5.0 % for 30-day exposure time (Table 40). For concentration from 1.0 % to 5.0 % for 3-day and 7-day exposure times and from 2.0 % to 5.0 % for 15-day exposure time the reduced corrosion rates are in the decreasing order as the concentration increases with a few exceptions. The 5.0 % concentration of corobit EPA-529 shows abnormally accelerated corrosion rate for a 30-day exposure, a rate that surpasses that for the blank waters in the corresponding situation.

The % inhibition efficiency of the corobit inhibitor for the urea cooling waters is the most with 0.1 % concentration for the 3-day and 7-day exposure times and 0.2 % concentration for 15-day and 30-day exposure times. With rising concentration, the inhibition efficiency decreases and becomes the least with 0.5 % concentration for 3-day and 7-day exposure times and 1.0% for 15-day exposure time and 2.0 % for 30-day exposure time. With increasing concentration from 1.0 % to 5.0 %, the inhibition efficiency improves for 3-day and 7-day exposure periods and from 2.0 to 5.0 % for a 15-day exposure time.

For higher concentrations of 1.0 %, 2.0 % and 5.0 % of the corobit inhibitor, the % inhibition efficiency decreases as the exposure time increases and becomes worst or negative with the 30-day long exposure. As against this, with lower concentration of the corobit inhibitor, the inhibition efficiency increases with prolonging exposure time; of course there are a few exceptions. In other words, the concentration of the corobit inhibitor plays an important role and perhaps a delicate balance has to be struck if the highest efficiency is desired, as revealed by this study.

The pH values of the urea plant cooling waters for various concentrations of the corobit inhibitor and different exposure times present quite interesting pattern, almost similar to the one for the ammonium sulphate plant cooling waters. The varying pH values are all in the alkaline range. The maximum inhibition efficiency exhibited by the 0.1 % concentration for 3-day and 7-day exposures, is in the pH range of about 8.1; that by 0.2 % concentration for 15-day and 30-day exposures, again about 8.1 pH. It appears that the maximum inhibition efficiency for the corobit inhibitor is associated with a pH range of about 8.0. As the pH value rises to 8.4 or so, the inhibition efficiency is the least for a 3-day and 7-day exposure periods. With longer exposure periods of 15 days and 30 days, the pH range for the least inhibition efficiency rises to 8.8 and 9.3 respectively. With prolongation of the exposure time, a rising pH is rather detrimental to inhibition efficiency, but with medium exposure time, the detrimental effect seems to be confined to the 8.5 pH range or so. Increasing pH and increasing exposure times and high concentrations of the corobit inhibitor are the negative factors as far as the urea plant cooling waters of GSFC Baroda, are concerned.

Caprolactum plant cooling waters are less corrosive as such, as compared to the ammonium sulphate plant and urea plant cooling waters. The effect of corobit EPA-529 inhibitor on cooling waters of this plant is comparable to that of the previous three cooling waters. It is interesting to note that the corrosion rates are very much reduced by the inhibitive effect of the corobit inhibitor. The most reduced corrosion rates are with 0.1 % concentration of the inhibitor for all the exposure times without exception. The least reduction in corrosion rates is experienced with 0.5 % concentration of the inhibitor for 3-day, 7-day and 15-day exposure times and with 1.0 % concentration for 30-day exposure time. It should be noted that the corrosion rates are very much reduced for all concentrations and exposure times studied under this investigation with the exceptions of 0.5 % and 1.0 % concentration for 15-day exposure and 0.5 %, 1.0 % and 2.0 % concentrations for 30-day exposure time when the corrosion rates are greatly accelerated. It is also accelerated in the case of 5.0 % concentration for 15-day exposure. However, the decreasing corrosion rates are not all in the same order. The reduced corrosion rates are in the increasing order as the concentration is increased from 0.1% to 0.5% for all the exposure times except that for the 30 day exposure time when increasing order is stopped by 2.0% concentration of the corobit inhibitor. After the maximum corrosion rate, though reduced, the corrosion rates alternately are low and higher for the 1.0%, 2.0% and 5.0% concentrations for all the exposure times.

Table 84

Difference in Corrosion Rate

Corrosion rate in mpy	Exposure time in days 3	7	15	30
Blank waters caprolactum plant	3.61	4.19	3.06	2.76
0.1% concentration	0.93	0.78	0.51	0.42
Difference	2.68	3.41	2.55	2.34

It can be seen from Table 84, that the difference in values of the corrosion rates for the blank and 0.1 % concentration cooling waters is about 2.7 which is not much different from the difference values except that for the 7-day exposure time. It means that the effectivity in cutting down the corrosion rate with 0.1 % concentration is almost the same for all the exposure times except for the 7-day exposure when it is the maximum.

Table 85

Comparison with the Urea plant cooling waters:0.1% concentration of the Corobit inhibitor

Corrosion rate mpy	Exposure time in days 3	7	15	30
Urea cooling waters	1.41	0.92	0.74	0.59
Caprolactum cooling waters	0.93	0.78	0.51	0.42
Difference	0.48	0.14	0.23	0.17

The comparison of the effectivity of 0.1 % concentration of the corobit EPA-529 for the urea plant cooling waters with that of the caprolactum plant cooling waters is given in Table 85; from the difference values of the corrosion rates for 0.1 % concentration of the inhibitor, it is clear that the inhibitor is more effective for the caprolactum cooling water system than for the urea plant cooling waters.

The maximum inhibition efficiency is thus exhibited by 0.1 % concentration of the corobit inhibitor. This inhibition efficiency increases as the exposure time increases without exception. The least efficiency is given by the 0.5 % concentration in the caseof 3-day and 7-day exposure times. For the 15-day and 30-day exposure times, 0.5 % and 1.0 % and 0.5 %, 1.0% and 2.0 % concentrations give accelerated corrosion rates; obviously these concentrations are prohibitive for inhibition purpose. After the least inhibition efficiency concentration, the inhibition efficiency further increases as the concentration increases with an exception of 2.0% concentration for a 3-day exposure where it is slightly less than that either for 1.0 % or 5.0 % concentration. The 5.0 % concentration again gives an accelerated corrosion rate for a 15-day exposure time and a negligible efficiency for a 30-day exposure time. The obvious conclusion is that higher concentrations of the corobit EPA-529 inhibitor has more damaging impact. The effect of concentration is very well seen by the contrast of about 85.0 % inhibition efficiency of 0.1 % concentration for a 30 day exposure and the accelerated corrosion efficiency of 0.5 to 2.0 % concentration on the one hand and just 3.6 % inhibition efficiency of 5.0 % concentration. The high corrosion efficiency indicates a good chemical activity, the only factor which can catch the eye is that of the pH which is quite high beyond 9, alongwith the exposure time. It appears that while high pH at the initial exposures provides the inhibition, at longer exposures, it is instrumental in enhancing corrosion. Long exposure in a high alkaline pH medium should be working in the direction of loosening the adherence of the protective film resulting into its passing into the aqueous environment at least partly. In that event, further surface exposure will permit the chemical activity resulting into enhancing the corrosion rate.

The case of make-up water and corobit-EPA-529 inhibitor is also interesting; it provides for explanation regarding part of the corrosion activity since it is mixed with the plant cooling water periodically to make-up the losses. In this case also, 0.1 % concentration turns out to be a better inhibition inducing amount excepting the 30-day exposure time where the best inhibition is given by 1.0 % concentration of the corobit inhibitor.

Table 86

Make-up water : Difference values in Corrosion Rates 0.1 % concentration of Corobit EPA-529

Corrosion rates mpy	Exposure time in days 3	7	15	30
Blank water	5.40	4.04	3.46	3.75
0.1 % concentration	2.32	1.65	1.15	2.51
Difference values	3.08	2.39	2.31	1.24

It is easily seen that the corrosion rates are greatly reduced by addition of corobit-EPA-529 inhibitor. As the concentration of the inhibitor increases, the decrease in corrosion rates follows a sort of alternating pattern, though the overall reduction in the corrosion activity is well maintained, with the exceptions of 0.2 % and 0.5 % concentrations for 15-day exposure period and 5.0 % concentration for 30-day exposure time. While this alternating pattern of variation in corrosion rates is not uniformly followed, what strikes most is the decreasing efficiency of inhibition as the concentration increases. In Table 86 is given the differentiating pattern of the effect of 0.1 % concentration over the inhibition accorded by the corobit inhibitor. It is seen that the difference values of the reduced corrosion rates are in the decreasing order of increasing exposure time. This means that as the exposure time increases, the protecting film on the surface of the metal becomes thick and does not get loosened so as to pass into the aqueous environment.

The inhibition efficiency for 0.1 % concentration of the corobit inhibitor increases as the exposure time increases except for the 30-day exposure time where it is greatly reduced - even the maximum inhibition efficiency in the case of 30-day exposure which is given by 1.0 % concentration is much lower than the inhibition efficiency given by 0.1 % concentration for 15-day exposure. The next very regular feature is the minimum inhibition efficiency which is given by 0.2 % concentration of the corobit inhibitor, for all the exposure periods. In this case, the inhibition efficiency has the reverse order; the minimum inhibition efficiency decreases as the exposure time increases with negative efficiency for a 15-day exposure period. Except for these two regular changing patterns, one of increasing efficiency in the maximum range with increasing exposure time, and the other of decreasing efficiency in the minimum efficiency range with increasing exposure time, for all other concentrations and exposure times, different patterns are observed.

The make-up water is basically alkaline when steel specimens are dipped into it for different exposure timings, its pH changes from 7.70 (fresh) to 8.48 (specimen exposed) after a 30-day exposure period. The chemical activity that takes place between the metal surface and the corrosive aqueous environment makes the environment not only to retain its alkalinity, but increases its alkalinity with increasing exposure time. Thus, the corrosive activity in the make-up water under investigation is carried on in the alkaline condition. With the addition of the corobit inhibitor, it is observed that the pH values become higher as the concentration increases as well as the exposure time increases. The chemical activity is providing inhibition is again one such where the environment (aqueous) retains the basic character and with changing concentration and exposure time, the basic character of the aqueous environment also changes. The maximum pH values are for the 5.0 % concentration for almost all exposure times. It is of interest to note that the maximum inhibition efficiency in this case is shown between approximately 8.8 and 9.0 pH values of the aqueous medium while the lower inhibition efficiency happens to be, on an average, below about 8.8 pH.

Corobit EPA-529, sold commercially as 'corrosion' and 'scale inhibitor' for open re-circulating cooling water systems, is basically a high molecular weight complex of organoamine phosphonates with specific additives such as zinc and dispersing agents. It is known for high sequestering value at threshold levels. Obviously, its high inhibitive power is to be attributed to the additives and their characteristics and sequestering property besides its capacity to form a stable film with the metal surface. A combination of organophosphonate and zinc works synergestically to give very good corrosion protection by interfering with the cathodic reaction (134-136). Organophosphonate with zinc give good protection without leading to any sludge formation (137). Due to the sequestering ability of phosphonates, the zinc ions present in a complexed form limiting the rate of reaction of zinc with hydroxyl ions. Therefore, useful concentration of zinc retained in solution for longer time and the slow deposition rate of zinc hydroxide allows the formation of a thin hydroxide film at the surface (138) giving desired corrosion resistance. The pH of the liquid corobit EPA-529 is 10.0; when added to the make-up water, the pH is 7.70 as reported in Table 42. The overall effective range of pH is found to be from 8.0 to 9.0 in different cooling waters taken for the present study. In Table 87 are given the effective pH range for all the five cooling waters.

Table 87

Effective pH range

pH rnage approximately	Cooling waters				
	Ammonia plant	Ammonium sulphate plant	Urea plant	Caprolactum plant	Make-up
Most effective	8.0-8.1	8.0-8.2	8.1-8.2	8.5-8.6	8.8-9.0
Least effective	9.0 & above	8.4-8.8	8.4-8.8	8.8-9.1	8.2-8.6 & above 9.0

In Table 88 is given a comparative evaluation in terms of % inhibition efficiency at the specific concentration of the corobit inhibitor for all the exposure times. It can be easily seen that by and large the most efficient concentration is 0.1 %. In fig.17 is given the % inhibitor efficiency by 0.1 % vol/vol corobit EPA-529 at various exposure days.

Table 88

Comparative Evaluation

Inhibition Efficiency

Cooling waters	Maximum Inhibition Efficiency (%) Concentration (%) of Inhibitor Exposure times in days 3	7	15	30
Ammonia plant	0.1	0.2	0.5	0.2
Ammonium sulphate plant	0.1	0.1	0.1	0.1
Urea plant	0.1	0.1	0.2	0.2
Caprolactum plant	0.1	0.1	0.1	0.1
Make-up	0.1	0.1	0.1	0.1

It may also be noted that while 0.2 % concentration of the corobit inhibitor works better in some exposure times, the margin is still in favour of 0.1 % concentration. In otherwords, except for one place where as much as 0.5 % concentration is needed to achieve high efficiency, 0.1 % concentration achieves the best that the corobit inhibitor can offer; this also is the economically a favourable point.

The maximum efficiency achieved differs from cooling water to cooling water and summary is given in Table 89 for at a glance review:

Table 89

Maximum Efficiency in %

Cooling water plants	Exposure time in days			
	3	7	15	30
Ammonia	100.0	98.07	99.06	99.64
Ammonium sulphate	70.41	75.47	81.63	88.92
Urea	78.51	81.19	87.10	86.63
Caprolactum	74.24	81.38	83.33	84.78
Make-up	57.04	59.16	66.76	33.07

The minimum efficiency ranges from 1.0 % to 52.0 %, the accelerated corrosion rates or negative efficiency is not taken into account though it is found in all at 11 different concentrations and exposure times.

The corobit inhibitor whose sequesteration value is 300 mg/gm can have consideration for scaling and fouling though the chelation of the organophosphate of the corobit with Ca of the waters may be undergoing in these cooling waters. This reaction may be contributing to the pH variations. Thus an indirect effect may be seen in affecting the corrosion inhibition efficiency due to pH variations. What is important, however, is the chemisorbed complex layer of the organophosphates over the steel surface and its adherence power. It would appear as if there is sufficient trapping of the H^+ ions from the cooling waters in the entire process of chemisorbed layer formation over the metal surface and chelation activity with the Ca^{++} ions in the aqueous medium, leaving behind OH^- ions in good number so as to enhance the pH values. While this may seem hypothetical at the moment, any detailed study in this direction was unwarranted due to specified objective of this investigation.

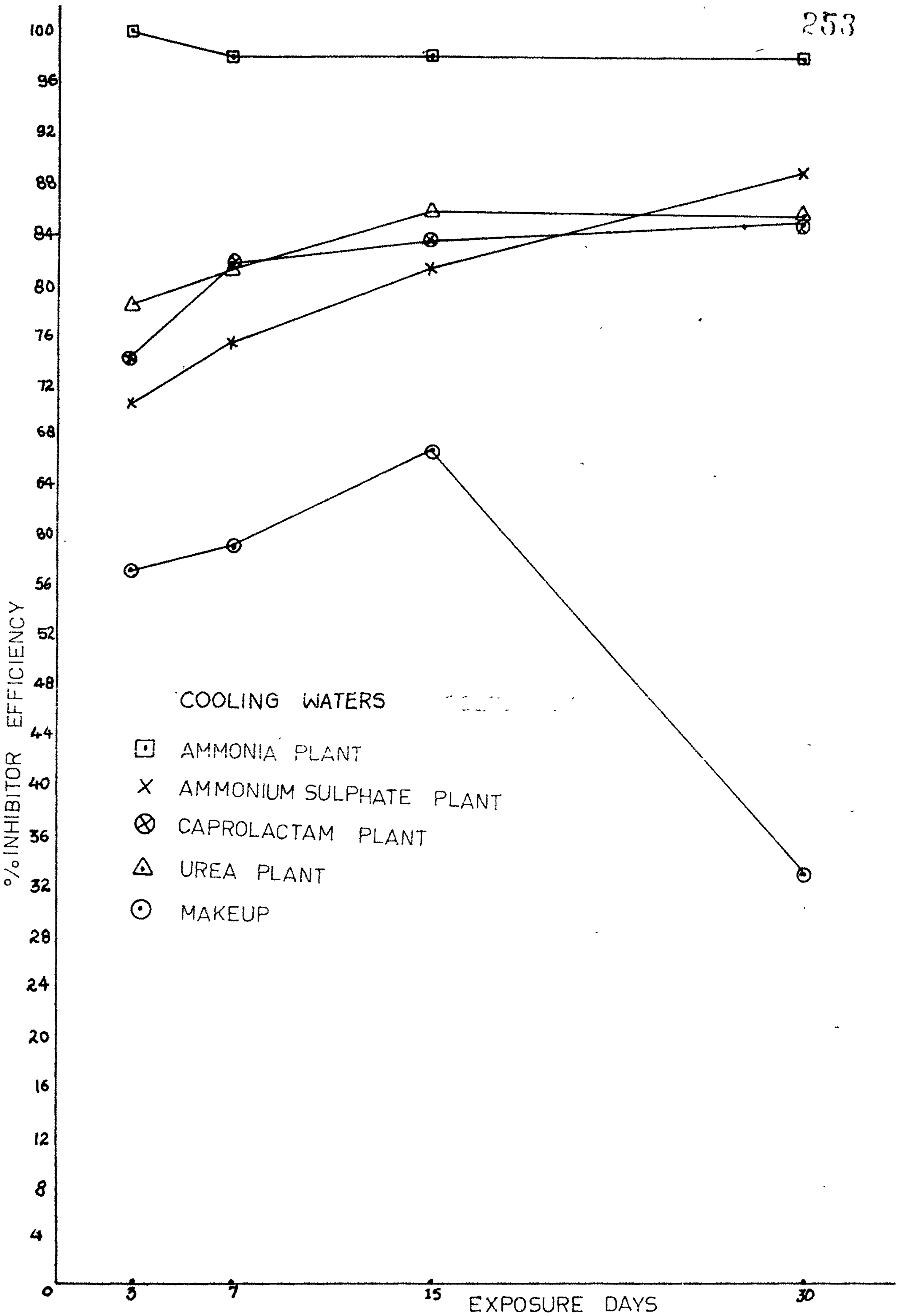


FIG 17 COOLING WATER WITH 0 1% VOl/VOl COROBIT EPA-529

(iii) Aquacid-105

The behaviour of aquacid is rather strange. It may be difficult to designate it an 'inhibitor' of corrosion. As such aquacid can have a direct comparison with the previous corobit EPA-529 inhibitor, an aspect which will be dealt with a little later. Right now, its behaviourism in ammonia plant cooling waters is examined; the observed corrosion rates are so strange that the claim of aquacid as an inhibitor can be jeopardy.

With 0.1 % concentration of aquacid in ammonia plant cooling waters, the corrosion rate increases from 1.41 to 9.18 for a 3-day exposure period. It is observed that (Table 43) the corrosion rate increases as the concentration of aquacid inhibitor increases for all exposure times, but for every individual % concentration, the corrosion rate falls as exposure time increases. In Table 90 are given the difference values of the increased corrosion rates with increasing % concentration of the aquacid inhibitor.

Itis easily seen that the corrosion rate for blank ammonia plant cooling water, which is within the 'mild' or 'negligible' range, is lifted up to a 'moderate' one with 0.1 % and 0.2 % of aquacid and becomes simply excessive with 0.5 % concentration. With 1.0 % to 5.0 % it is

Table 90

Difference Values of Corrosion Rates

3-day Exposure	Blank		% concentration 0.1		0.2		0.5		1.0		2.0		5.0
Corrosion rate mpy	1.41		9.18		14.42		38.55		74.79		149.09		281.35
Difference value		7.77		5.24		24.13		36.24		74.30		132.26	
7-day Exposure													
Corrosion rate mpy	1.14		3.97		7.41		19.03		36.92		70.17		109.90
Difference values		2.83		3.44		11.62		17.89		33.25		39.73	
15-day Exposure													
Corrosion rate mpy	1.80		2.34		4.10		10.23		14.32		24.39		65.32
Difference value		0.54		1.76		6.13		4.09		10.07		41.93	
30-day Exposure													
Corrosion rate mpy	2.77		1.68		2.21		5.54		7.86		13.01		24.58
Difference value		1.09		0.53		3.33		2.32		5.15		11.57	

extraordinarily enormous. It proves beyond doubt that aquacid for ammonia plant cooling waters cannot function as inhibitor on the contrary it can save, if need be, as an extraordinary corrosive agent.

In this case of accelerated corrosion, it is observed that the impact of increasing concentration is greater than that of increasing exposure times, as discerned from the difference values of corrosion rates derived in Table 90. The difference in corrosion rates between 0.1 % and 0.2 % becomes less and less as the exposure time from 3-day period increases to 7-day, 15-day and 30-day periods; the difference values are 5.24, 3.44, 1.76 and 0.53. These decreasing corrosion rates are insignificant as compared to the increasing corrosion rates with increasing % concentration from 0.1 % to 5.0 %, the difference values being 5.24, 24.13, 36.24, 74.30 and 132.26 respectively for a 3-day exposure time, 3.44, 11.62, 17.89, 33.25 and 39.73 respectively for 7-day exposure time, 1.76, 6.13, 4.09, 10.07 and 41.93 respectively for 15 day exposure time and 0.53, 3.33, 2.32 5.15 and 11.57 respectively for 30-day exposure. Just as the number of days of exposure increases, the difference values in the corrosion rates as the % concentration increases, slump down (Table 43). However, apparently it seems to be working as inhibitor for 0.1 % and 0.2 % concentration for a 30-day exposure time, but it seems to be illusion, since a lot of corrosion has already taken place and the slowing down of the corrosion rate may due to a period of passivity that might have set in after a tremendous corrosion rate prior to reaching a 30 day exposure level. Yet a striking feature is that the corrosion rates from 0.1 % to 5.0 % concentrations of the aquacid for a 3-day exposure period get reduced seven to ten times less correspondingly for a 30-day exposure time. Obviously a kind of passive environment does seem to develop as the time of exposure is prolonged resulting into a tremendous cut down in the corrosion rates.

The ammonia plant cooling waters, pretreated as they are, show an alkaline range of pH between 7.39 to 8.4 for all the exposure times. As soon as even 0.1 % aquacid is added, the pH value falls to 2.74 for a 3-day exposure period; simultaneously as noted above, the corrosion rate is enhanced by about seven times that of the corresponding blank rate. Decrease in PH value, or in other words, conversion of alkaline medium to acidic with the addition of 0.1 % aquacid, the corrosion rate is enormously enhanced. However, the corrosion rate has been found to be decreasing for the particular concentration, as the exposure time increases. It is now noted that as the exposure time increases, the pH value also increases and crosses 7 value by 30-day exposure period. It is thus possible to link the increase of pH value with the decreasing corrosion rate.

The rates lower than that of the blank waters are given by 0.1 % and 0.2 % concentrations for 30-day exposure time; the pH values of the aqueous environment in these cases are either slightly alkaline or nearing neutral level. This would suggest that the greater the acidic nature of the aqueous environment, the higher will be the corrosion rates in the case of aquacid as inhibitor.

The ammonium sulphate plant cooling waters are more corrosive than ammonia plant cooling waters; the blank water corrosion rates are about four times higher. With the addition of 0.1 % aquacid, the corrosion rates in this case also are enhanced rather than depressed. But, the extent of enhancement is much different, as seen in Table 91.

Table 91

Extent of Escalation in Corrosion

Cooling waters	Corrosion rate in mpy	Time of Exposure in days 3	7	15	30
Ammonia plant	Blank	1.41	1.14	1.80	2.77
	0.1 % concentration	9.18	3.97	2.34	1.68
	Difference	7.77	2.83	0.54	*1.09 (decrease)
Ammonium sulphate plant	Blank	5.61	4.81	4.41	4.06
	0.1 % concentration	10.95	7.36	5.60	4.05
	Difference	5.34	2.55	1.19	* 0.01 (decrease)

From the difference values for the corrosion rates as derived in Table 91, it can be seen that these values are less comparatively in the case of ammonium sulphate cooling waters except for the higher exposure time of 15 and 30 days. It is also observed that with increasing concentration, the corrosion rates increase in the same abnormal manner and decrease as the exposure time increases for all concentrations of the inhibitor. The pattern of varying corrosion rates against changing concentrations and exposure times is almost the same as that observed for the ammonia plant cooling waters. All the corrosion rates are highly accelerated except that due to 0.1 % concentration for 30-day exposure, which is only a little less than that for the blank one, viz with 0.25 % inhibition efficiency.

The pH values of the ammonium sulphate plant cooling waters comparable with those for the previous cooling waters (blank); with the addition of aquacid in varying amounts, the overall scene of the changed pH values, now well within the acidic range, is also comparable. The pH values are all in the acidic range, except some which can be said to be nearing neutral or negligibly alkaline. The corrosion rates are the highest when the aqueous medium is highly acidic.

The same strange behaviour of aquacid continues with urea plant waters. However, the extent of corrosion intensity is a little bit less than those exhibited by either of the two previous cases. Here again, the corrosion rate increases as the % concentration of aquacid increases. It also increases as the exposure time increases; but taking into consideration a single concentration versus different exposure times at a time, it is possible to asert that the corrosion rates decreases as the exposure time increases though the decreased rates are sufficiently higher than the corresponding blank corrosion rates except in four cases, viz. 0.1 % concentration for 7, 15 and 30 days exposure periods and 0.2 % concentration for 15 and 30 days exposure times, when the corrosion rates are somewhat lower than those for the corresponding blank rates. It is in these exceptions that % inhibition efficiency is 32.52, 65.42 and 78.47 for 0.1 % concentration for 7 day, 15 day and 30 day exposure time respectively and 12.90 and 26.49 for 0.2 % concentration for 15 day and 30 day exposure periods respectively. It can be said that where inhibition efficiency is exhibited by aquacid inhibitor, it increases with increasing exposure time and decreases with increasing concentration.

The varying pH values for uaea plant cooling waters with and without aquacid for all the exposure periods are given in Table 45. Their variation pattern is comparable with those for the first two cooling waters. Where the aqueous environment after adding aquacid assumes most acidic range, the corrosion are the highest. In these exceptional cases where aquacid has displayed inhibition efficiency, the pH range is either nearing neutral level ~~or~~ is alkaline, though only slightly.

In the case of caprolactum plant cooling waters, the role of aquacid inhibitor is the same as before. Its presence in these cooling waters is as corrosive as it could be. With 0.1 % of the aquacid, the blank water corrosion rate of 3.61 mpy for a 3-day exposure period rises to become 10.08 mpy. From 'mild' to 'moderate' corrosion with just 0.1 % concentration of the so called inhibitor aquacid is something not aimed at. It is further observed (Table 44) that the corrosion rate increases as the concentration increases to 5.0 % and can be termed as 'high' or 'excessive'. For each concentration the corrosion rates decrease as the exposure time increases; the pattern of decreasing corrosion rate is almost similar to those observed earlier, for the aquacid 'inhibitor'.

While in the case of the previous three cooling waters, aquacid did show inhibition efficiency occasionally, say with 0.1 % and 0.2 % concentrations for a 30-day exposure period for ammonia plant cooling waters, 0.1 % concentration for a 30 day exposure for ammonium sulphate plant cooling waters and 0.1 % for 7 day, 15 day and 30 day exposure periods and 0.2 % for 15 day and 30 day exposure periods for urea plant cooling waters, for caprolactum plant cooling waters, it just works as a corrosion agent.

The pH values from clearly alkaline range for blank waters for all exposure periods change to distinctly acidic range with addition of aquacid and the pH values decrease as the % concentration of aquacid increases. With the increasing exposure periods, the pH values increase, but hardly any reaches the neutral or slightly alkaline range at which a little inhibitive property of aquacid can be expected.

The case of aquacid with make-up waters is no different. The corrosion rates increase as the concentration of aquacid increases - the rates become more vigorous at the highest concentration. However, with 0.1 % concentration, the inhibition action is seen for 7-day, 15 day and 30 day exposure periods. In this case, the corrosion rates decreases as the exposure time increases, giving quite high inhibition efficiency (Table 47). While corrosion rates decrease as the exposure time increases for almost all other concentrations except 0.1 % concentration, the reduced corrosion rates are never less than that for the corresponding blank waters. Though in decreasing sequence, the rates display excessive corrosive tendency of the aqueous environment with addition of aquacid. It is of somewhat interest to note that though the presence of aquacid result into excessively accelerated corrosion rates excepting the three instances cited above, the overall corrosion rates are in a corresponding comparative assessment, in this case, somewhat lesser than the rates found in other cooling waters taken for the study.

The pH values shrink to the acidic range with addition of aquacid to the make-up water. As the concentration of aquacid increases, the pH values decrease, The pH values, however, show a pattern of increasing sequence as the exposure time increases. One more point of interest is that with lower concentration of aquacid but with higher exposure time, the pH values increase more than those corresponding with higher concentration. The make-up waters are the third more corrosive of the lot of five cooling waters selected for the study; the first being urea plant cooling waters, the second, ammonium sulphate plant cooling waters, the fourth, caprolactum cooling waters and the fifth, ammonia plant cooling waters. Against this sequence of the original characteristics, on addition of aquacid to these waters, with the highly enhanced corrosion rates in almost all the five cases, the least corrosive is the make-up water.

(vi) Diammonium hydrogen ortho phosphate

The stock of cooling waters is now a different one collected from all the plants as well as the make-up water since the original stock was consumed in the study of the previous three inhibitors. This part is an extended study, take-up for verifying impact of this important material. Therefore, their blank corrosion rates for all exposure times will be different from those already considered so far. The ammonia plant cooling waters are in this new stock, more corrosive than the previous stock. The blank corrosion rate for a 3 day exposure time is 3.80 mpy; as the exposure time increases the blank corrosion rate decreases. However, the extent of decrease in the corrosion rate is the least between 7 days and 15 days exposure, as discerned from the difference values in the decreased corrosion rates given in Table 92. In other words it means that the corrosiveness is more during this period as compared to either the initial or the highest exposure time.

Table 92

Extent of decrease in corrosion rates vs exposure time

	Corrosion Rates : mpy Exposure time in days						
	3		7		15		30
Corrosion rates: mpy	3.80		3.43		3.25		2.84
Difference		0.37		0.18		0.41	

The fourth inhibitor taken for study under this investigation is diammonium hydrogenortho phosphate-DAP. With the presence of diammonium hydrogen orthophosphate, the corrosion rates are decreased to a good extent. The maximum corrosion rates are exhibited by 0.2 % concentration with the exception of the 30 days exposure when it is by 0.1 % concentration of DAP. The minimum corrosion rates are with 2.0 % concentration of DAP for all exposure time except that for a 3 day exposure when it is with 1.0 % concentration of the inhibitor. It is easily seen that with the highest corrosion rate (though decreased sufficiently), the % inhibition efficiency will be the lowest and with the lowest corrosion rates, the % inhibition efficiency will be the maximum. It appears that a 2.0 % concentration is the most appropriate concentration to obtain the best results with DAP for this cooling water. However, it should be noted that with just 0.1 % concentration of DAP, the corrosion rates are reduced to a great extent and the inhibition is quite high. The difference values of the blank corrosion rates and those with 0.1 % concentration of DAP are given in Table 93 which speak for themselves.

Table 93

Ammonia cooling waters : Difference values of corrosion rates

Concentration of DAP	Corrosion rates mpy Exposure time in days 3	 7	 15	 30
Blank	3.80	3.43	3.25	2.84
0.1 % concentration of DAP	0.67	1.22	0.90	1.03
Difference values	3.13	2.21	2.35	1.81

The difference values, in terms of % inhibition efficiency, of the highest and the lowest corrosion rates with DAP as inhibitor, are given in Table 94. From these difference values, it becomes clear that the impact of concentration

Table 94

Difference in % inhibition efficiency with DAP

% Inhibition efficiency	% Inhibition Efficiency Exposure time in days 3	 7	 15	 30
Lowest	35.0	37.90	30.15	63.73
Highest	95.26	96.21	98.92	98.94
Difference	60.26	58.31	68.77	35.21

is considerable and that it can not be ignored even if economic considerations were to lead to other conclusion.

The pH values of the ammonia plant blank cooling waters are in the alkaline range (Table 48). The pH values, however, rise and fall alternately with the exposure time. There are besides, two more interesting observations. First, the concentration of the inhibitor DAP increases, the pH values increase from 7.07 (blank) to 8.36 (2.0% concentration) for the fresh solutions. Second, for every concentration of the DAP inhibitor, the pH values decrease as the exposure time increases. The % inhibition efficiency also increases as the concentrations of the inhibitor DAP as well as the exposure time increase; in one case, it is a relationship of increasing pH and in the other, that of decreasing pH.

The new stock of ammonium sulphate plant cooling waters is less corrosive than the previous stock, as seen from the blank corrosion rates for all the exposure times (Table-51). The corrosion rates for the blank waters decrease with increasing exposure time as given in Table 95.

Table 95

Effect of decrease in corrosion rate versus exposure time

	Corrosion rate mpy Exposure time in days						
	3		7		15		30
Corrosion rate mpy	2.96		2.67		2.34		2.33
Difference		0.29		0.33		0.01	

The blank corrosion rate for 3-days exposure time is 2.96 mpy, as the exposure time increases blank corrosion rate decreases. However extent of decrease in corrosion rate is the least between 15 days and 30 days exposure, as discerned from the difference value in the decrease corrosion rate is given in Table 95. It is also shown in Table 51 that as the days passes water become alkaline and attain highest value 8.85 after 3 days from 7.47 to 8.85 and again shows fall as exposure days passes and attain the value of 8.29. The maximum corrosion rate was exhibited by 0.1 % DAP after 3, 7, 15 and 30 days. Minimum corrosion rate was observed with 2.0% DAP at 7 and 15 days except for 3 days by 1%. After 30 days exposure 1 % and 2% concentration shows weight gain which indicate protective film on the metal surface, which is so adherent and is difficult to remove by scouring agent. The pH value at all concentration decreases as the exposure time increases is shown in Table 51. It can be generalised that 2% DAP is appropriate for obtaining highest inhibitor efficiency. Considering economic aspect and for moderate protection 0.5 % concentration is quite encouraging which shows 97.26 % protection at 3 day.

The pattern of % efficiency of DAP with Ammonia plant and ammonium sulphate plant has some similarity at 3 days, in both the cases highest inhibitor efficiency is obtained by 1% at 3 days and at 7,15 and 30 days highest inhibition obtained with 2% DAP (Table 48 and 51).

Comparing inhibitor efficiency of 1% DAP it can be seen from table 96 that at all the exposure periods the inhibition efficiency is higher in ammonium sulphate plant cooling water compare to ammonia plant cooling water.

Table 96

Comparison for 1.0 % DAP Efficiency in reducing corrosion rates of ammonium sulphate cooling waters and ammonia cooling waters.

	% Inhibition efficiency Exposure time in days			
Cooling waters	3	7	15	30
Ammonia plant	95.26	95.32	79.69	91.19
Ammonium sulphate plant	97.03	97.38	94.87	wt.gain
Difference in inhibition efficiency	1.77	2.06	15.18	-

Now from above results it is clear that with increasing number of days difference in efficiency increases, at 30 days in ammonium sulphate plant coupon shows weight gain indicating protective film on metal surface. Overall protection given by DAP in ammonium sulphate plant cooling waters is quite good compare to ammonia plant cooling water.

The change of pH pattern in ammonia plant cooling water (Table 48) and ammonium sulphate plant cooling water (Table 51) is also similar as exposure days increases pH decreases at all concentrations of DAP. This indicate possibility of passing of H^{+} ions into solution after film formation has taken place releasing H^{+} ions.

Now third cooling water taken for study is he cooling water of caprolactum plant. The heighest inhibition efficiency achieved by 1 % DAP in caprolactum plant is mentioned in table 49. The pattern of change in pH at all the concentrations with varying exposure days is similar with ammonia and ammonium sulphate plant cooling water.

It can be seen from Table 97 that the efficiency obtained by caprolactum plant at 0.1 % concentration is quite high compare to ammonium sulphate plant cooling water as shown in Table 97.

Table 97

Comparision of 0.1 % efficiency in reducing corrosion rate of ammonium-sulphate plant cooling water and caprolactum plant cooling water

	Inhibition efficiency Exposure time in days			
Cooling water	3	7	15	30
Caprolactum plant	92.51	82.06	75.97	76.57
Ammonium sulphate plant	31.76	46.07	39.74	61.37
Difference in inhibition efficiency	60.75	35.99	16.23	15.20

It is observed from the table 97 that protection afforded to metal increases with increase in exposure time in ammonium sulphate plant as difference in efficiency decreases. The corrosion rate for the blank water with increasing exposure time for caprolactum plant is given in Table 98.

Table 98

Effect of corrosion rate versus exposure time

	Exposure time in days						
	3		7		15		30
Corrosion rate mpy	3.74		2.62		5.16		3.97
Difference in corrosion rate mpy		1.12		2.54		1.19	

The difference in the corrosion rates derived from table 98 may be compared with those derived in table 95. At a glance it can be seen that the difference value in corrosion rates in table 98 are greater than the corresponding values given in table 95, indicating thereby that the blank rate of caprolactum cooling waters are much higher. Eventhough the protection afforded has meagre difference compare to overall efficiency of ammonium sulphate plant.

It is seen from (Table 49) that 0.1 % DAP is enough to achieve the maximum efficiency after 3 days. This favour economic cum lesser time aspects for better protection in shorter duration to achieve maximum passivation. Another important aspect to be considered that adhesive film formation takes place with 1% and 2 % concentration in caprolactum plant cooling water and ammonium sulphate plant cooling water after 30 days exposure which can give life long protection to heat exchangers from corrosion damage. The fourth water taken for the study was urea cooling water, from (Table 50) it is clear that with increasing number of exposure days there is decrease in corrosion rate of blank water. The corrosion rate are so negligible that it seem us water itself, has inhibiting property. It is also observed that higher concentration of 0.5, 1 and 2 % shows acceleration corrosion rate at 15 days. Similarly at 2 % concentration shows acceleration in corrosion rate after 3 days. Overall inhibition efficiency is found greater at 7 days with all the concentrations compare to 3, 15 and 30 days exposure. From Table 99 it is clear for blank that there is decreasing trend of corrosion rate with increasing time, indicating passivating film become compact as the exposure time increases.

Table 99

Extent of corrosion rate versus exposure

	Exposure time in days						
	3		7		15		30
Corrosion rate mpy	0.24		0.14		0.060		0.028
Difference in corrosion rate		0.10		0.080		0.032	

The poor inhibition at 15 days may be attributed to the fact that there will be formation of film which increases protection upto 7 days but with increasing time above 7 days the film may be thicken heavily and may fall by gravity and again fresh metal exposed to inhibitor which afford new protection between 15 days to 30 days span, and which gives good efficiency at 30 days as shown in (Table 50). Again it is observed from (Table 50) with increasing concentration after 3 days gives poor corrosion may be due to excess ammonia of DAP to existing ammonical nitrogen imparts high alkalinity to water, accelerate corrosion. Later on there is improvement in inhibition efficiency may be due to removal of ammonia with time and formation of passivating film. From Table 50 it is evident that pH change has some effect on % inhibition efficiency particularly at 15 days. At first two concentrations i.e. 0.1 and 0.2 % where pH first decreases on 3, 7 and 15 days but on 30th day it increases, the results of % inhibition efficiency (on 15 day) are negative. The only reason be for deviation in % inhibition efficiency can be assigned as the effect of pH change between 15 and 30 days span.

The fifth water taken for study with DAP is make-up water. From Table 100 it is observed that there is rise of corrosion rate by 0.14 from 15 to 30 days, while there is fall in corrosion rate by 0.52 at 3 days, and 1.05 at 7 days.

Table 100

Extent of corrosion rate versus exposure time blank make-up water

	Corrosion rate in mpy Exposure time in days						
	3		7		15		30
Corrosion rate in mpy	3.15		2.63		1.58		1.72
Difference in corrosion rate		0.52		1.05		0.14	

Similarly it is observed that there is fall of pH between 7 and 15 days by 0.25 and sudden increase of pH by 0.20 from 15 to 30 days in blank water as shown in Table 101.

Table 101

Extent of pH change versus exposure time blank make-up water

	Change in pH Exposure time in days						
	3		7		15		30
pH	8.87		8.73		8.38		8.58
Difference in pH		0.14		0.25		0.20	

As seen from table 101 increase in pH from 15 to 30 day by 0.20, indicate the passing of hydroxyl ion into the medium or in other words the corrosion products adhered to metal surface which was blocking chemical reaction, has been broken and shows degradation of metal surface by chemical reaction of metal with water.

In makeup water from (Table 52) it is clear that at 0.1% and 0.2 % concentration of DAP there is poor inhibition efficiency. But with 0.5, 1 and 2 % concentration of DAP inhibition efficiency is very good. At 3 days and 7 days exposure maximum efficiency was obtained with 1 % DAP and at 15 and 30 days the inhibition efficiency was achieved highest by 2 % DAP. If we assess the (Table 52) horizontally it is observed that 0.1, 0.2, 0.5 and 2% give highest protection after 30 days while 1% DAP give highest efficiency at 15 days. From economic aspect it is advisable to adopt 0.5 % DAP concentration where also efficiency of 90 % can be achieved and for any process plant with limited concentration to have better efficiency is a positive factor.

In Table 102 is given a comparative evaluation in terms of % inhibition efficiency at the specific concentration of the DAP inhibitor for all exposure time. It can be easily seen that by and large the most efficient concentrations are 1 and 2 %.

Table 102

Comparative evaluation inhibition efficiency

Cooling waters	Maximum inhibition efficiency (%) concentration % of inhibitor Exposure times in days			
	3	7	15	30
Ammonia plant	1	2	2	2
Ammonium sulphate plant	1	2	2	1&2
Urea plant	0.5	2	0.2	0.1
Caprolactam	1	1	1	1&2
Makeup	1	1	2	2

The maximum efficiency achieved differs from cooling water to cooling water and a summary is given in table 103 for at a glance review.

Table 103

Maximum efficiency in %

Cooling water plants	Exposure time in days			
	3	7	15	30
Ammonia	95.26	96.21	98.92	98.94
Ammonium sulphate	97.91	97.38	94.87	wt.gain
Urea	29.17	57.86	28.33	57.14
Caprolactum	95.19	97.06	96.12	wt.gain
Makeup	96.98	96.31	97.85	98.60

The minimum efficiency ranges from 5.0 to 20.0 %, the accelerated corrosion rates or negative efficiency is not taken into account though it is found in all at 4 different concentrations and exposure times. At four places in all shows weight gain for which 100 % efficiency is taken into consideration. The graphical representation for % inhibition efficiency at various concentrations of DAP at 30 days exposure is given in (Fig.18).

Now from this study it is clear that DAP can offer better protection to heat exchanger, as well as from toxicity point of view also it is a very good corrosion inhibitor. Buttler (139) believes that orthophosphate in presence of divalent ions gives cathodic protection. Phosphate form tenacious film on the mild steel surfaces as a result it is applied for prefilming of various equipment from corrosion damage (59). The mechanism of phosphate as corrosion inhibitor in water has been extensively studied by polish worker (140). As per their opinion the mechanism is a function of the form of phosphate ion and $H_2PO_4^-$ combines with the Ca^{+2} and Mg^{+2} usually present in the water to form a lyophobic colloid which will adsorbed in the cathode region of the metal surfaces. Study by Comeaux (141) and Murray (142) suggest the deposition of cathodic film limits the diffusion of oxygen to metal water interfaces and the precipitation of insoluble ferric compound over anodic sites. From our study of anodic polarisation curve of DAP it is supporting the above facts that orthophosphate protect metal by cathodic inhibition (fig.22,23).

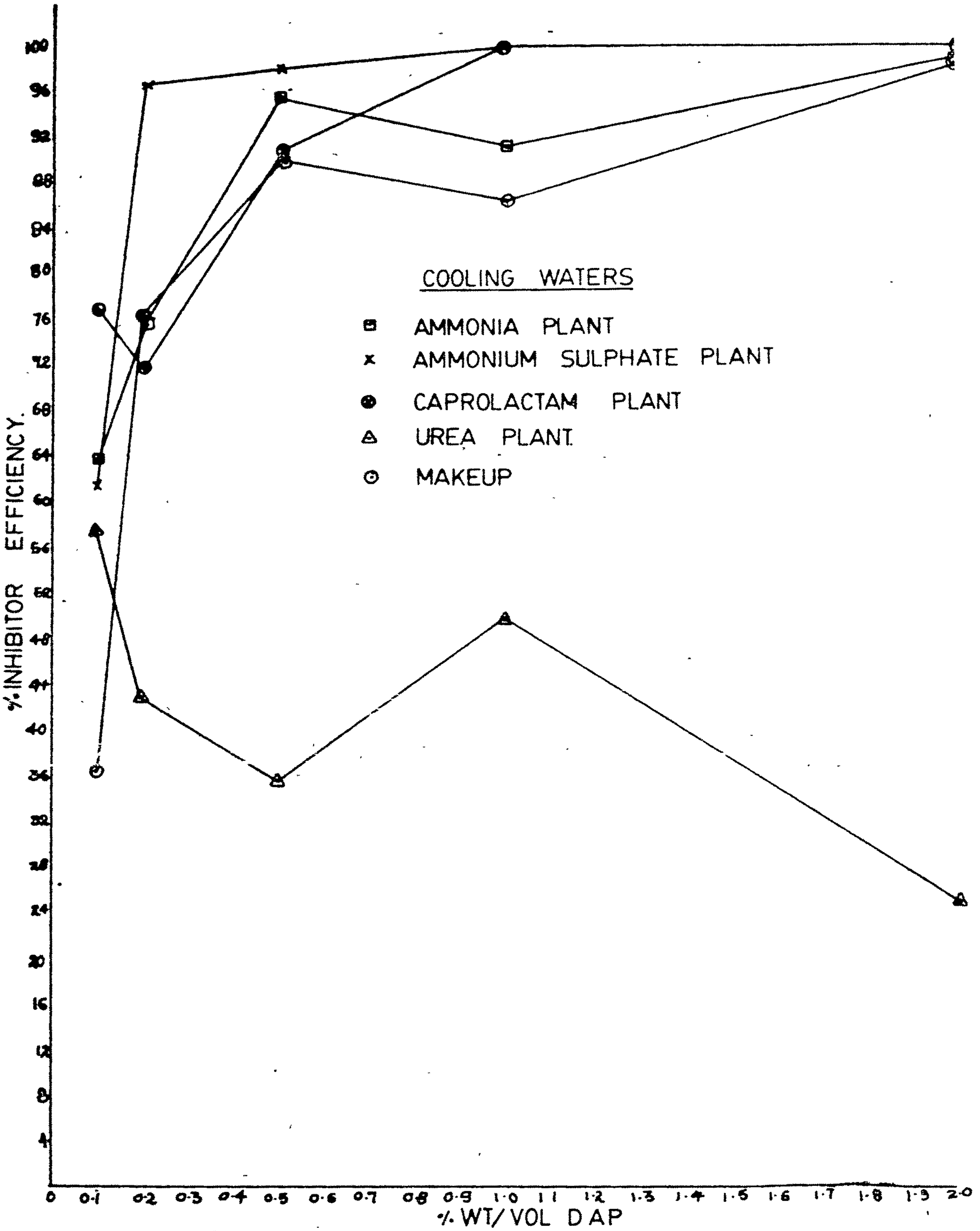


FIG. 18 DAP - 30 DAYS EXPOSURE.

(v) Aquacid-105 + DAP

For this study new lot of cooling waters were taken except makeup water the analysis of which is given in table 28-32, this is a extended part of study to evaluate the mixed system of Aquacid-105 + DAP.

Looking to the behaviour of mixed system from corrosion rate it is observed that behaviour of mixed system is quite strange. It may be difficult to designate this system as an inhibitor of corrosion. As such mixed system can have a direct comparison with the previous study as discussed for aquacid and DAP alone. Right now, its behaviourism in ammonia plant cooling water is examined, the observed corrosion rates are so strange the claim of mixed system as an inhibitor can be jeopardy.

With 0.1 % Aquacid + 0.1 % DAP in ammonia plant cooling water, the corrosion rate increases for a 3 day exposure period from 3.26 to 8.27 mpy. It is observed that (Table 53) the corrosion rate decreases as concentration of DAP increases from 0.1 % to 0.5 % at all the exposure time. But increase of concentration of 1% DAP increases corrosion rate at all the exposure time compare to 0.5 % DAP. This favour optimum concentration of 0.5 % DAP with 0.1 % aquacid gives better protection as shown in (Table 53). But for every individual % concentration of mixed system i.e. 0.1 % Aquacid + 0.1 % DAP

0.1 % Aquacid + 0.5 % DAP, 0.1 % Aquacid + 1% DAP the corrosion rate falls as exposure time increases. In Table 104 are given the difference value of corrosion rate with increasing % concentration of DAP in 0.1 % aquacid.

Table 104

Difference value of corrosion rate

	% concentration (Aquacid-105+DAP)			
	Blank	0.1+0.1	0.1+0.5	0.1+1
3 days exposure				
Corrosion rate mpy	3.26	8.27	5.39	7.24
Difference value		+5.06	-2.88	+1.85
7 days exposure				
Corrosion rate	3.37	3.08	3.07	3.73
Difference value		-0.29	-0.01	+0.66
15 days exposure				
Corrosion rate	1.89	1.67	1.32	1.70
Difference value		-0.22	-0.35	+0.38
30 days exposure				
Corrosion rate	2.62	1.18	0.90	1.09
Difference value		-1.44	-0.28	+0.19

(+) - indicate increase in corrosion rate
(-) - indicate decrease in corrosion rate

It is easily seen that the corrosion rate for blank ammonia plant cooling water, which was in 'mild' or 'negligible' range, is lifted upto moderate one after 3 days exposure. It is also clear from the table-104 that with 0.1 % Aquacid + 1 % DAP there is higher corrosion rate compare to 0.1 % Aquacid + 0.1 % DAP and 0.1 % Aquacid + 0.5 % DAP mixture. It is also seen from previous study of Aquacid, alone that aquacid has tendency of accelerating corrosion rate initially than decreases gradually with exposure time, as is true in this system also but addition of DAP has reducing accelerating power of Aquacid.

In the same water with 5 % Aquacid + 0.1 % DAP, 5 % Aquacid + 0.5 % DAP and 5 % Aquaicd + 1 % DAP there is acceleration in corrosion rate but corrosion rate reduces vertically and horizontally as the exposure time increases. The difference in corrosion rate can be visualised from Table 105.

From (table 53) it is clear that corrosion rate was found less in a system of 5 % aquacid + 1% DAP compare to 5 % aquacid + 0.1 % DAP and 5 % Aquacid + 0.5 % DAP at 30 days exposure period. Another important observation is the increase of PH trend in 0.1 % Aquacid + 0.1 % DAP, 0.1 % Aquacid +.0.5% DAP and 0.1 Aquacid + 1% DAP from initial pH to the exposure of 3 days and 7 days but shows fall in pH at 15 and 30 days.

Table 105

Difference value of corrosion rate

	% Concentration (Aquacid+DAP)						
	Blank		5+0.1		5+0.5		5+1
3 days exposure							
Corrosion rate in mpy	3.26		206.25		180.12		173.05
Difference		+202.99		-26.13		-7.07	
7 days exposure							
Corrosion rate in mpy	3.37		109.11		99.36		86.70
Difference		+105.74		-9.75		-12.66	
15 days exposure							
Corrosion rate in mpy	1.89		32.32		41.27		35.55
Difference		+30.43		-8.95		-5.72	
30 days exposure							
Corrosion rate in mpy	2.62		26.19		33.46		22.05
Difference		+23.57		-7.27		-11.14	

(+) - Indicate increase in corrosion rate

(-) - Indicate decrease in corrosion rate.

It is also observed that with increasing exposure days thickness of the film also increases i.e. at 30 days exposure, compactness in the film is superior.

The ammonium sulphate plant cooling waters are found corrosive at 3 days exposure compare to ammonia plant cooling waters. From difference in corrosion rate of 7, 15 and 30 days exposure it is clear that difference is nominal. By addition of 0.1 % Aquacid + 0.1 % DAP there is increase in corrosion rate in both the water at 3 day exposure but decreases with increase in exposure hours. From Table 106 it is clear that at 3 days exposure difference in corrosion rate was found 2.07 in ammonium sulphate plant compare to 5.01 in ammonia plant indicating good protection by 0.1 % Aquacid + 0.1 % DAP in ammonium sulphate plant compare to ammonia plant.

Table 106

Extent of Escalation in corrosion

Cooling waters	Corrosion rate in mpy	Time of exposure in days			
		3	7	15	30
Ammonia Plant	Blank	3.26	3.37	1.89	2.62
	0.1% Aquacid + 0.1% DAP concentration	8.27	3.08	1.67	1.18
	Difference	+5.01	-0.29	-0.22	-0.44
Ammonium sulphate plant	Blank	4.94	3.59	2.73	2.24
	0.1% Aquacid + 0.1% DAP concentration	7.01	3.38	1.85	1.73
	Difference	+2.07	-0.21	-0.88	-0.51

(+) - Indicate increase in corrosion rate
(-) - Indicate decrease in corrosion rate

It is clear from Table 106 that highest efficiency at 15 days in ammonium sulphate plant and at 30 days in ammonia plant at concentration of 0.1 % aquacid + 0.1 % DAP. The overall efficiency in ammonium sulphate plant by mixed inhibitor is low compare to ammonia plant. The maximum efficiency of 32.23 % is observed after 15 days with 0.1 % aquacid + 0.1 % DAP.

It is observed from (Table 56) that at all concentrations, the corrosion rates increases in the same abnormal manner and decreases as the exposure time increases. The pattern of varying corrosion rate and change in pH against changing concentrations and exposure times is almost same as for ammonia plant cooling waters.

The same strange behaviour of aquacid + DAP continues with urea plant waters. However, the extent of corrosion intensity is a little bit less than those exhibited either of the two previous cases. The highest inhibitor efficiency achieved at 0.1 % Aquacid + 1 % DAP at 30 days which is 83.47. The max. efficiency of 0.1% Aquacid + 0.1 % DAP and 0.1 % Aquacid + 0.5%DAP is also exhibited at 30 days which is 82.91 and 81.79 % respectively. The pattern of decrease in corrosion rate with increase in exposure time is almost same as of ammonia and ammonium sulphate plant except for 15 days with 0.1 % Aquaicd + 0.1 % DAP, 0.1% Aquacid + 0.5 % DAP and 0.1 % Aquacid + 1 % DAP. With

5 % Aquacid + 0.1 % DAP, 5 % Aquacid + 0.5 % DAP and 5 % Aquacid + 1 % DAP the pattern of decrease in corrosion rate with increase in exposure time is similar to ammonia and ammonium sulphate plant. The pattern of pH change has similar trend as in previous cases.

The fourth water taken for study is of caprolactam plant. Of all the waters evaluated with this sytem, the blank water of caprolactam plant was found more corrosive. The water shows corrosion rate of 6.69 mpy at 3 day. Corrosion rate decreases gradually with increase in exposure time. In other plant waters for 7, 15 and 30 days exposure time inhibitor efficiency obtained occasional with 0.1 % Aquacid + 0.1 % DAP, 0.1 % Aquacid + 0.5 % DAP and 0.1 % Aquacid + 1 % DAP. But with caprolactam plant with 7 days exposure highest efficiency of 59.77 % is achieved with 0.1% Aquacid + 0.5 % DAP. At 15 days highest efficiency of 70.49% was obtained at 0.1 % Aquacid + 0.5 % DAP. At 30 days highest efficiency with 0.1% Aquacid + 0.5 % DAP was observed 85.14%. Considering overall efficiency, 85.14% is the heighest efficiency achieved in caprolactam plant system. With increase in exposure time shows trend toward increase in efficiency except for 15 days with 0.1% Aquacid + 1% DAP concentration in caprolactam plant. The probable effective combination found in caprolactam system is 0.1% Aquacid + 0.5% DAP. The 5% Aquacid + 0.1% DAP, 5% Aquacid + 0.5% DAP and 5% Aquacid + 1% DAP shows decreasing trend of corrosion rate with increase in exposure time as in previous waters.

The behaviour of mixed system of aquacid +DAP is not much differing in makeup water from previous waters. Heighest efficiency with 0.1% Aquacid + 0.1% DAP is 68.27% and with 0.1% Aquacid + 0.5% DAP is 66.40% is observed at 30 day. Heighest efficiency with 0.1% Aquacid + 1% DAP is 47.98% is at 15 days (Table 57). In all the three concentrations 5% Aquacid + 0.1% DAP, 5% Aquacid + 0.5% DAP and 5% Aquacid + 1% DAP, maximum protection can be achieved after 30 days with 5% aquacid + 1% DAP with minimum corrosion rate of 21.28 MPY. In above concentrations there is decrease in trend of corrosion rate with increasing exposure hours.

In table-107 is given a comparative evaluation in terms of % inhibition efficiency at the specific concentration of the mixed (Aquacid + DAP) for all the exposure time.

Table 107

Comparative evaluation inhibition efficiency

Cooling water	Maximum inhibition efficiency (%) concentration(%) of inhibitor (Aquacid+DAP) Exposure time in days			
	3	7	15	30
Ammonia	N	0.1+0.5	0.1+0.5	0.1+0.5
Ammonium sulphate	N	0.1+0.1	0.1+0.1	0.1+0.5
Urea Plant	0.1+1	N	0.1+0.5	0.1+1
Caprolactam	0.1+0.1	0.1+0.5	0.1+0.5	0.1+0.5
Makeup	N	0.1+0.5	0.1+1	0.1+0.1

N-Negative efficiency

Maximum efficiency achieved differs from cooling water to cooling water and a summary is given in table 108 for at a glande review.

Table 108

Maximum efficiency in %

Cooling water plants	Exposure time in days 3	7	15	30
Ammonia	N	8.90	30.16	65.65
Ammonium sulphate	N	55.85	32.23	23.21
Urea	36.03	N	76.45	83.47
Caprolactam	7.77	59.77	70.49	85.14
Makeup	N	44.55	47.98	66.40

N-Negative efficiency

From over all comparision it is clear from table 107 that 0.1% Aquacid + 0.5% DAP is a suitable inhibitor in general. From table 108 it is concluded that over all protection by mixed system is higher in caprolactam water compare to other cooling waters. The higher protection was observed with longer exposure i.e. 30 days.

Generalising the mixed system study, it can be concluded that inhibition efficiency was found greater with DAP combination with 0.1% aquacid compare to 5% aquacid. The main ingredient of aquacid-105 is 1, hydroxy ethyledine, 1,1,diphosphonic acid, which has very good sequestering capacity, distortion property, defloculation property, threshold inhibition etc. It alsols protects the metal by adsorption mechanism forming chemisorbed layer on the metal surface. Addition of DAP to aquacid enhances its inhibition by imparting cathodic protection. At lower concentration 0.1% aquacid with DAP it is observed by polarisation curve it has cathodic nature (fig. 24,25), while 0.1% aquacid alone has mixed type of nature (fig. 24) which does not shows in shift potential toward cathodic or anodic direction. While polarisation curve of DAP shows cathodic inhibition (fig. 22, 23). So at lower concentration of 0.1% Aquacid + DAP inhibitor gives protection by adsorption and cathodic inhibition. It is also observed that with increase in exposure time film become more compact.

In 5% aquacid + DAP system, HEDP content available is more so it will sequester Ca^{+2} and Mg^{+2} or in otherwords hardness imparting ions and make water very soft i.e. aggresive for corrosion attack. The same is conformed by settling of solids at the bottom of beaker during experimentation. With 5% aquacid + DAP system in waters acidic pH was prevailing was also a factor for accelerating corrosion rate. In general for inhibition purpose more than 0.1% aquacid is not desirable with various % of DAP concentrations.

II. Effect of surface treatment on inhibitor efficiency with 2% wt./vol. Benzotriazole

With a view to explore the inhibitor efficiency of 2% benzotriazole with rough and smooth surface of mild steel specimen, the synthetic cooling water was taken and under same experimental conditions cited for inhibitor evaluations with five waters, the experiment was conducted. From (Table 58) it is clear that for blank synthetic water the corrosion rate of rough specimen (treated with IS grit-60) was quite high as compared to smooth specimen (treated with IS grit-240) at 3 and 7 days. This may be due to coarse surface having stresses, scratches etc. favour anodic site formation which leads to dissolution of metal by forming corrosion cell. But at 15 and 30 days the corrosion rate of blank water with rough surface was found less compare to smooth surface, this may be due to formation of protective layer on metal surface which prevent further dissolution of base metal. It is clear from experimental data (Table 58) that benzotriazole is having high efficiency at 3 days with rough surface compare to smooth surface. At 3, 7, 15 and 30 days the efficiency increases horizontally but decreases vertically in rough surface except 3 day as shown in (table 109). But in case of smooth surface the inhibitor efficiency with 2% benzotriazole increases horizontally at 3, 7, 15 and 30 days and increases vertically at 7, 15 and 30 days compare to rough surface. This may be due to the formation of polymeric complex with base metal.

Table - 109

2% wt./vol. Benzotriazole

Grit No.	% Inhibitor efficiency No. of exposure days			
	3	7	15	30
60	70.0	79.78	79.50	93.02
240	66.00	85.55	90.76	94.67

At 15 days the % inhibition efficiency was found higher by 11.26% in smooth surface compare to rough surface. At 30 days the % inhibition efficiency was found higher just by 1.26% in smooth surface compare to rough surface. Hence it is concluded that prolonged exposure of 2% benzotriazole to either rough or smooth surface will not show appreciable change in % inhibitor efficiency. It is also seen from (table 58) that with the same concentration i.e. 2% benzotriazole with blank water does not shows remarkable change in pH with exposure time either with rough or smooth surface. The % inhibitor efficiency vs exposure days is shown in Fig. 27.

III. Anodic Polarisation (Table 59)

To know the type of inhibitor, anodic polarisation curves were plotted using M-4100 potentiodyne analyser (fig. 12) at lowest and highest concentration using makeup water.

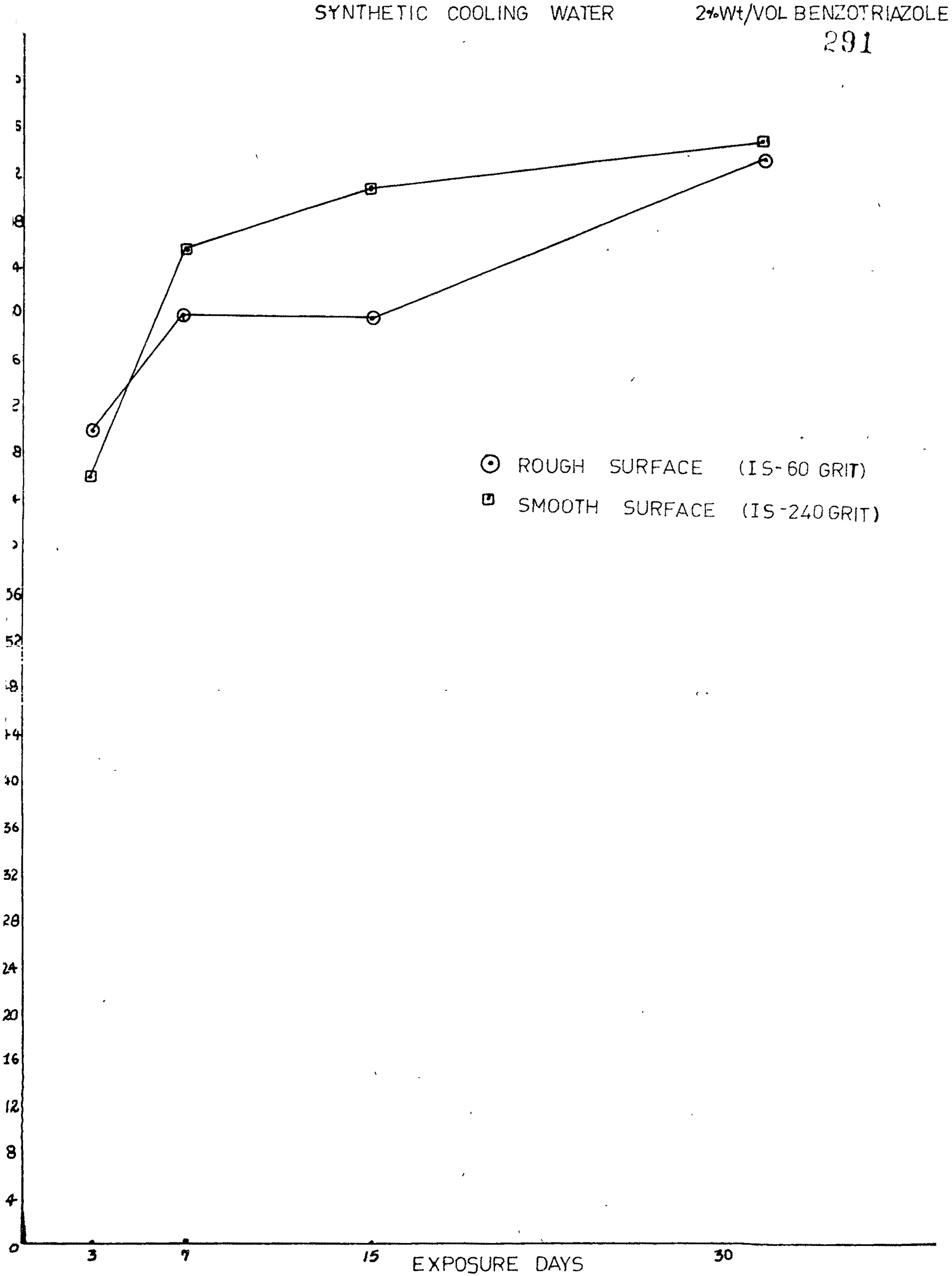


FIG. 27 EFFECT OF SURFACE TREATMENT WITH 2% BENZOTRIAZOLE

h-I Benzotiazole

Benzotriazole shifted the potential toward anodic direction with respect to blank water indicating that it is an anodic inhibitor to mild steel. The similar results were obtained by Zak (143) with potentiostatic polarisation curve and supported greater inhibition of anodic process. For 0.1% wt/vol. benzotriazole shift in potential was 480 mV in anodic direction and 2% wt/vol shows shift in potential by 520 mV toward anodic direction i.e. increase in concentration increase the shift of potential in anodic direction (fig. 19).

h-II Corobit EPA-529

Corobit EPA-529 shifted the potential toward cathodic direction with respect to blankwater indicating that it is cathodic inhibitor. 0.1% vol/vol corobit EPA-529 shifted the potential by 120 mv in cathodic direction and 5% v/v corobit EPA-529 shifted the potential by 180 mv in cathodic direction i.e. increase in concentration increase the shift of potential in cathodic direction which is shown by (fig. 20).

h-III Aquacid-105 (H.E.D.P)

In aquacid-105, 0.1% v/v did not shift the potential either towards anodic or cathodic direction i.e. curve super imposed the potential axis of blank water (Fig. 24). 0.2% v/v Aquacid-105 shifted the potential by 160 mv in anodic direction (Fig. 21) and 5% v/v aquacid-105 shifted the potential by 260 mv in anodic direction (Fig.26) with respect to blank. So increase in concentration from 0.1% changing its behaviour from mix to anodic type. Increase in concentration shift the potential in anodic direction.

h-IV Diammonium hydrogen orthophosphate

DAP shift the potential toward cathodic direction with respect to blank water, so it is a cathodic inhibitor. 0.1% wt/vol DAP shift 40 mv (Fig.22) and 2% wt/vol DAP shifted potential by 250 mv in cathodic direction (Fig. 23). Hence increase in concentration increase the shift toward cathodic direction.

h-V Aquacid-105 + DAP

Aquacid-105 (H.E.D.P) + Diammonium hydrogen orthophosphate in combination of 0.1% v/v + 0.1% wt/vol, 0.1 v/v + 0.5% wt/vol and 0.1 v/v + 1% wt/vol. shows shift in potential 100, 110, 130 mv respectively toward cathodic direction (fig. 24,25) which indicate with increasing concentration of DAP in aquacid-105 (0.1%) shows increase in shift toward cathodic site. This indicate in above mixture effect of DAP is more compare to aquacid-105. At higher concentration of aquacid-105 i.e. 5% v/v and 1% wt/vol DAP mixture shows shift in potential toward anodic side by 170 mv, which indicate anodic nature of the formulation. This also conforms the anodic nature of 5% v/v aquacid-105 as shown in (fig.26). Anodic shift as shown in (fig.26) of 260 mv by aquacid-105 was decrease to 170 mv by addition of 1% DAP as shown in (fig. 26). The addition of 1% DAP shifts 5% Aquacid potential toward cathodic direction by 90 mv.

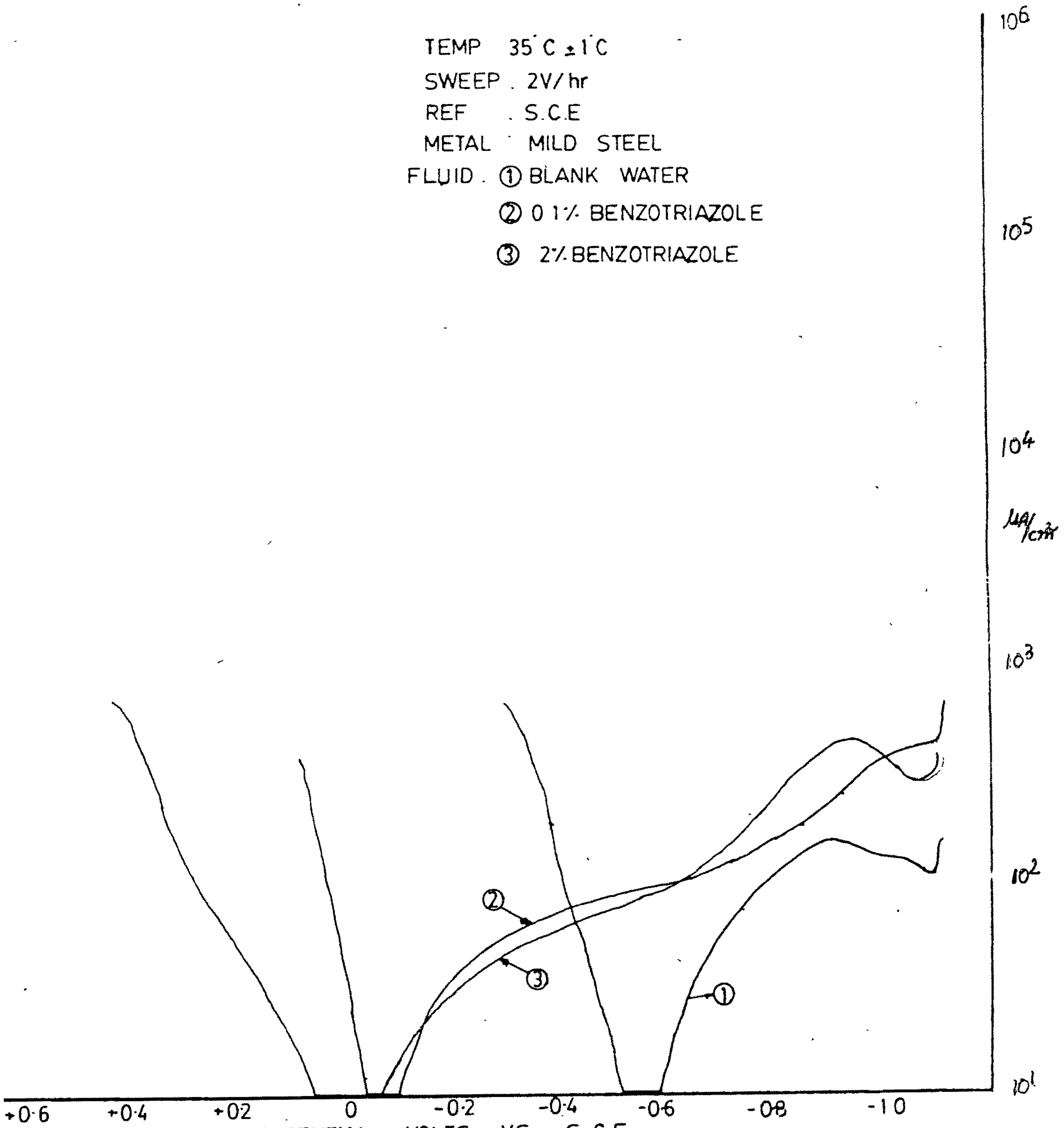


FIG. 19 POTENTIAL VOLTS VS. S.C.E.

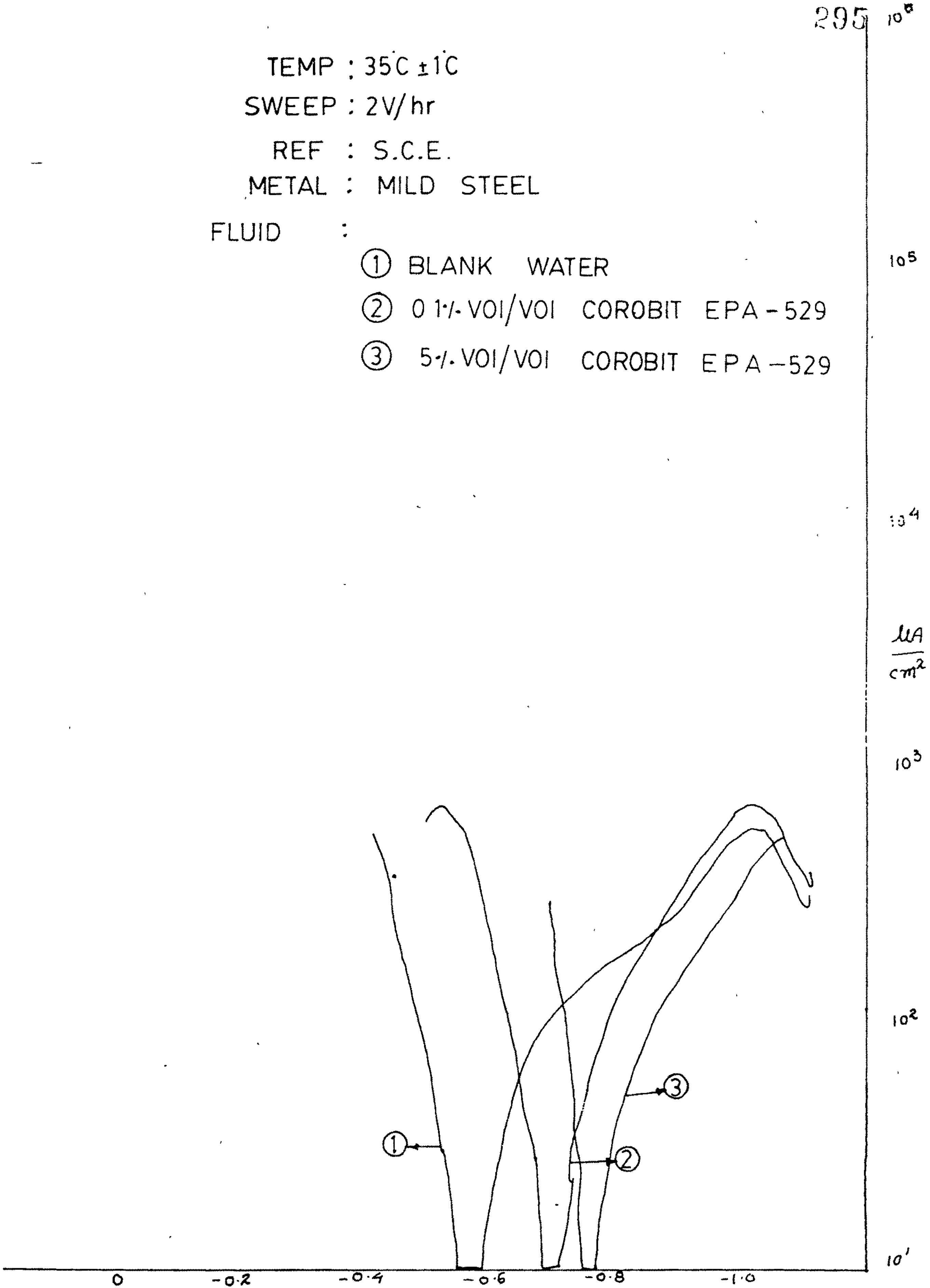


FIG.20 POTENTIAL VOLTS VS S.C.E.

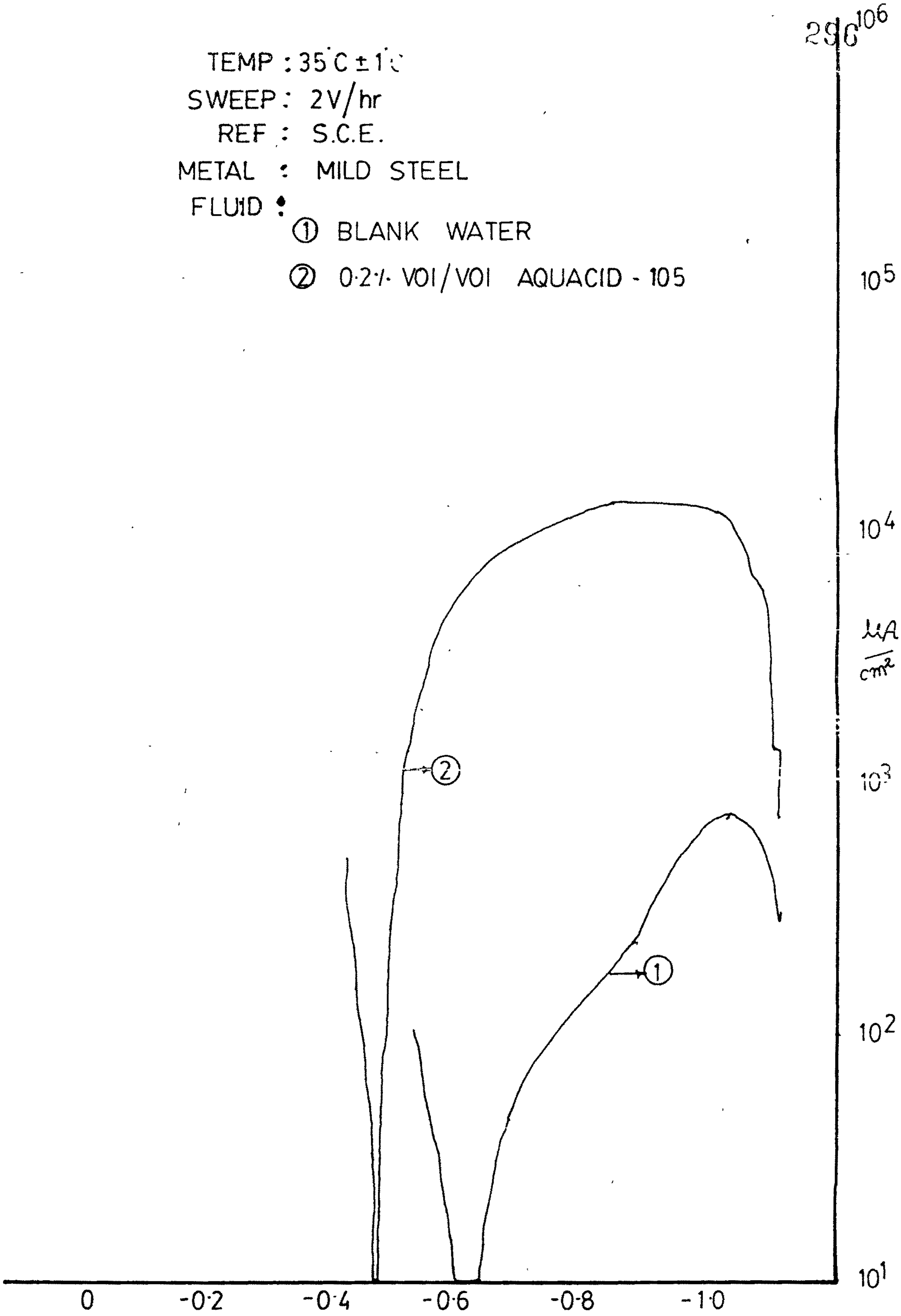


FIG. 21. POTENTIAL VOLTS VS S.C.E.

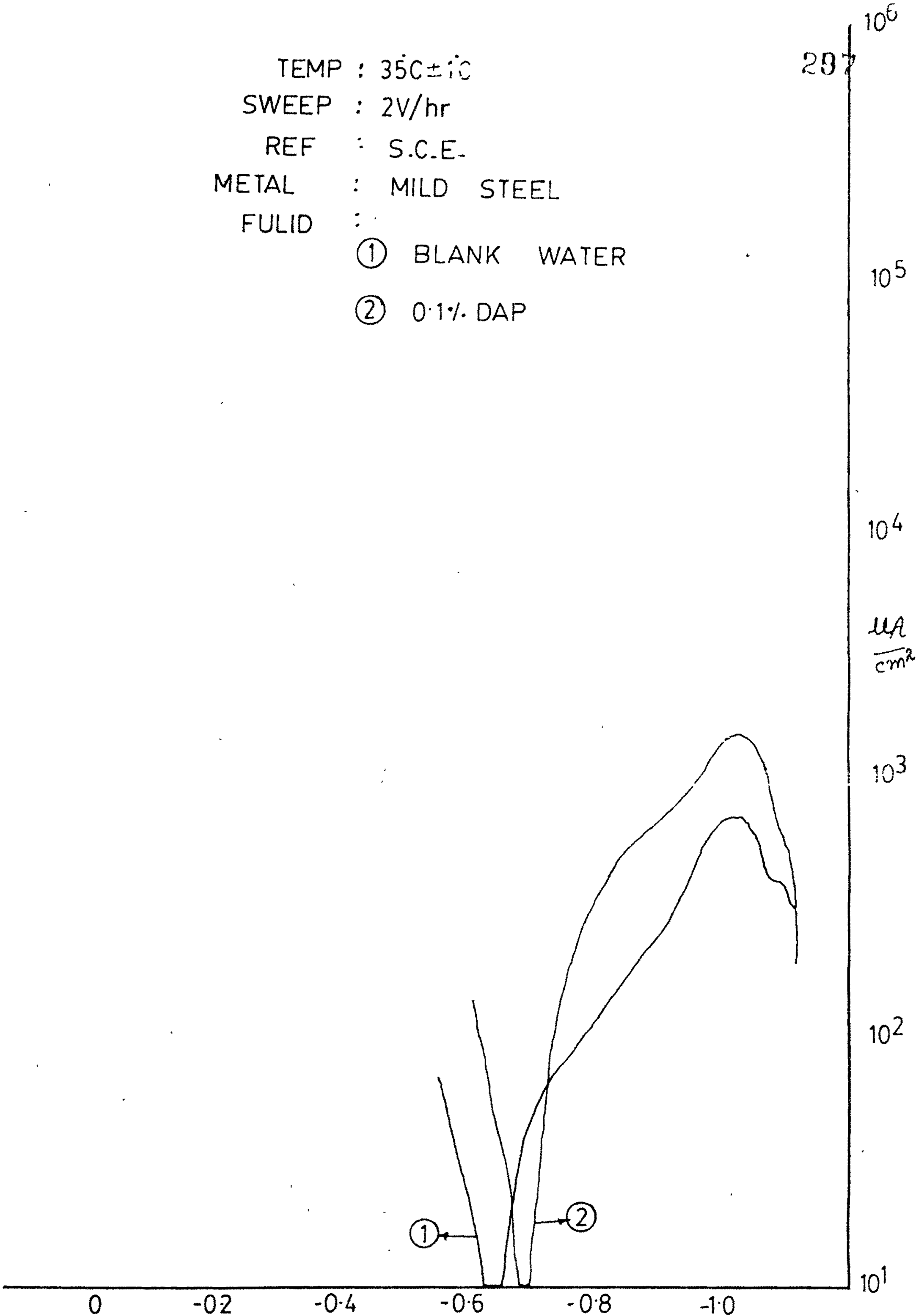

TEMP : 35C±1C
SWEEP : 2V/hr
REF : S.C.E.
METAL : MILD STEEL
FULID :
① BLANK WATER
② 0·1% DAP
10^6
10^5
10^4
μA/cm²
10^3
10^2
10^1
①
②
0
-0·2
-0·4
-0·6
-0·8
-1·0
POTENTIAL VOLTS VS S.C.E.

FIG. 22

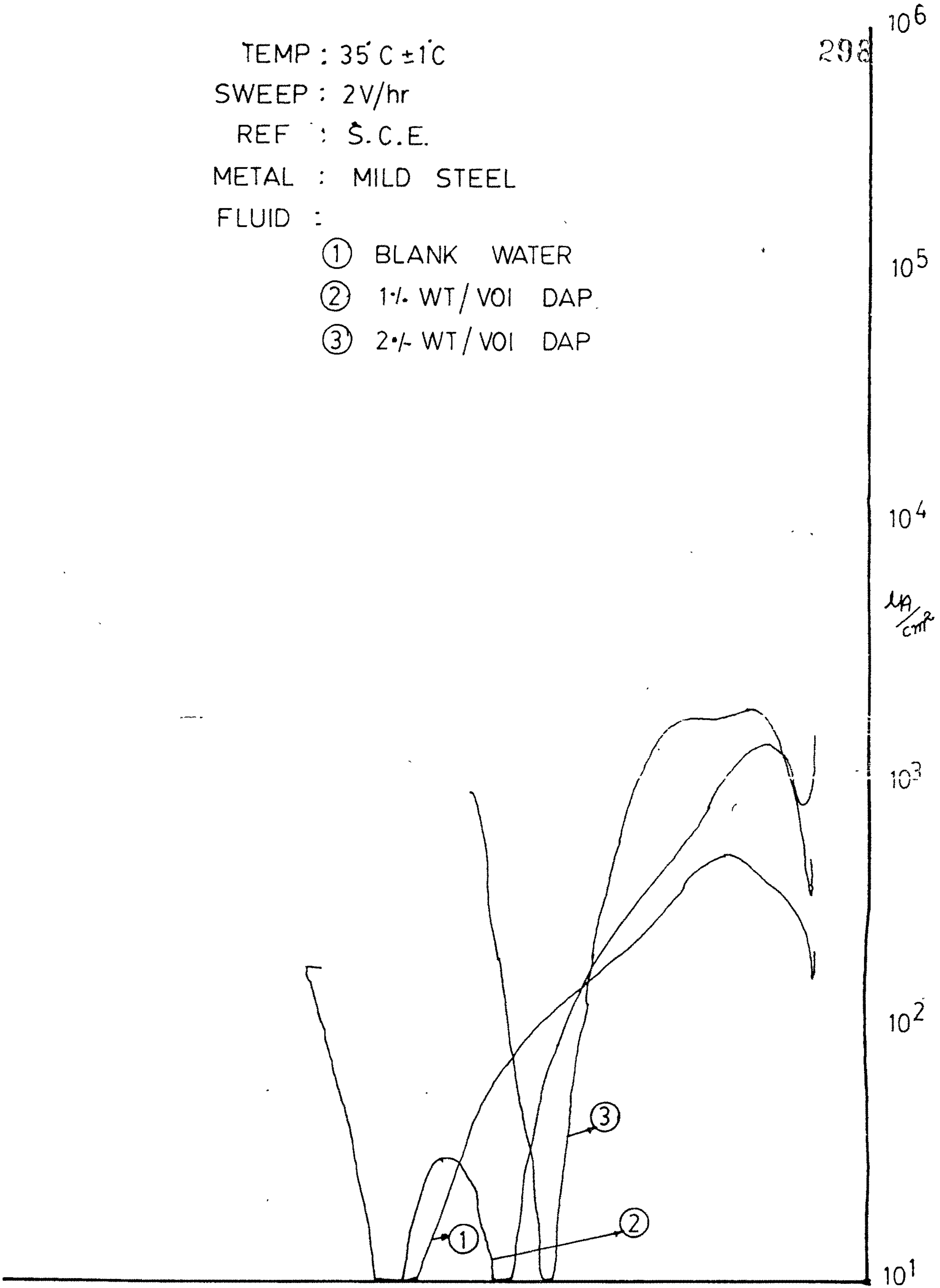


FIG.23 POTENTIAL VOLTS VS S.C.E.

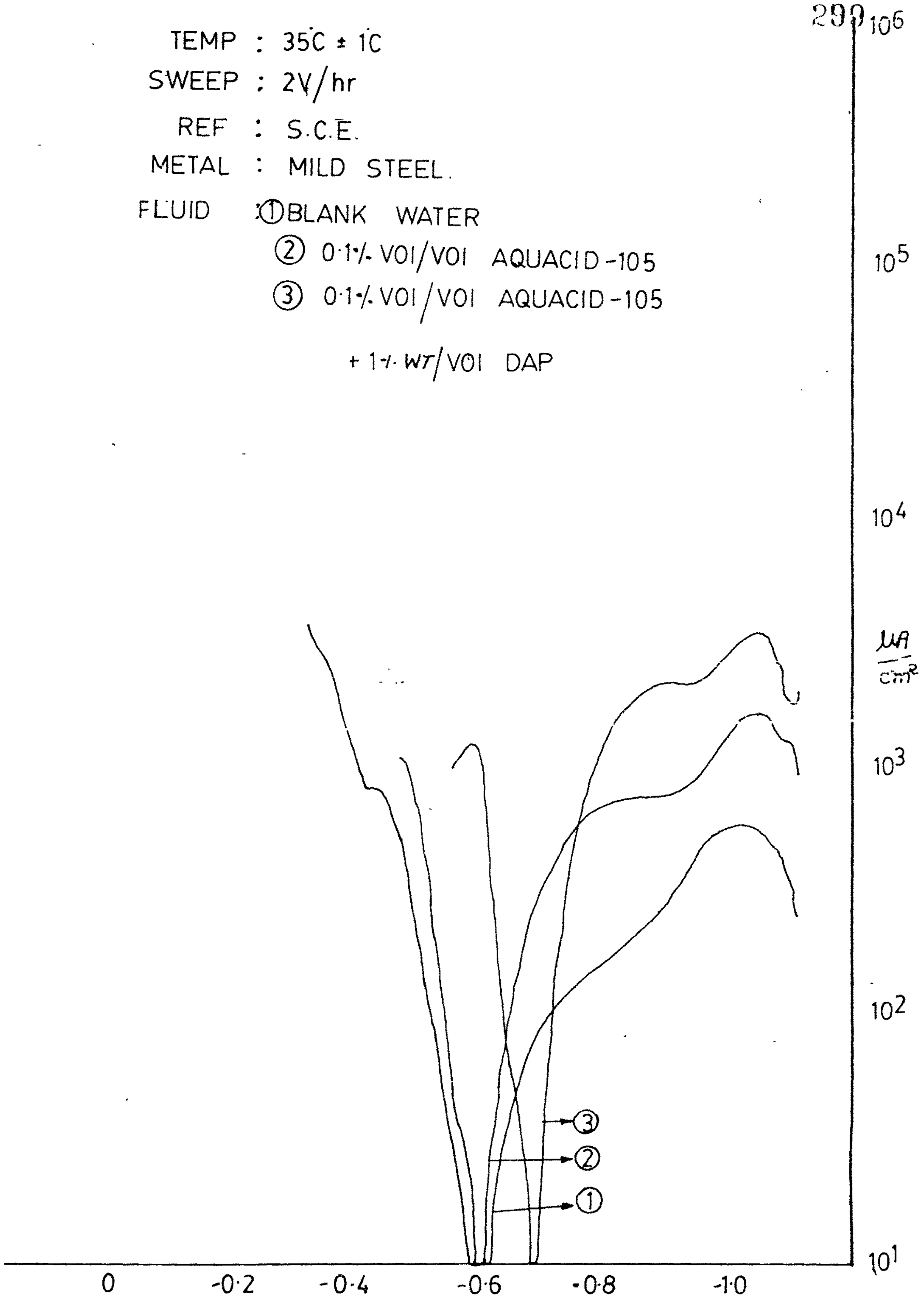


FIG.24. POTENTIAL VOLTS VS S.C.E.

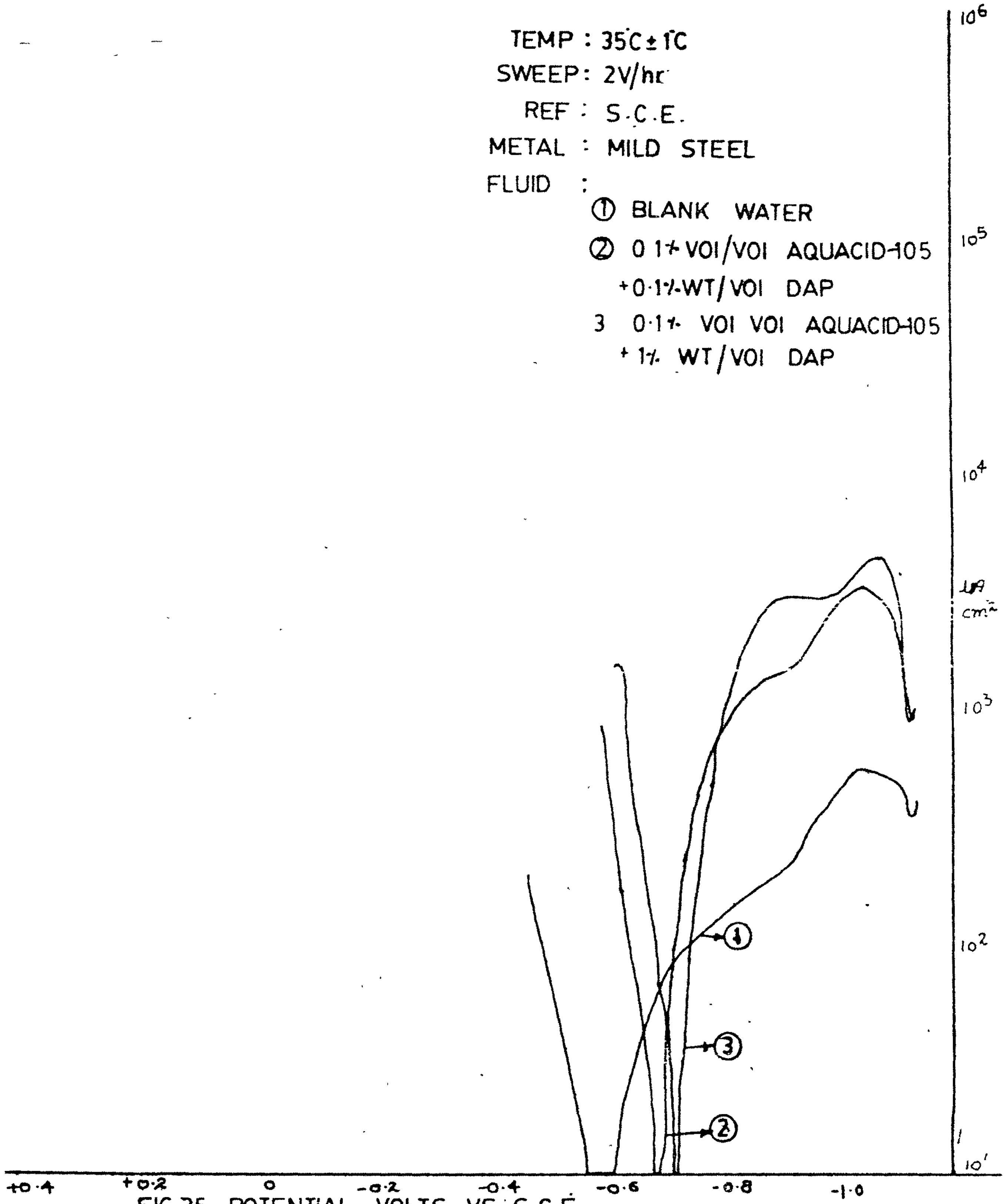


FIG.25 POTENTIAL VOLTS VS S.C.E.

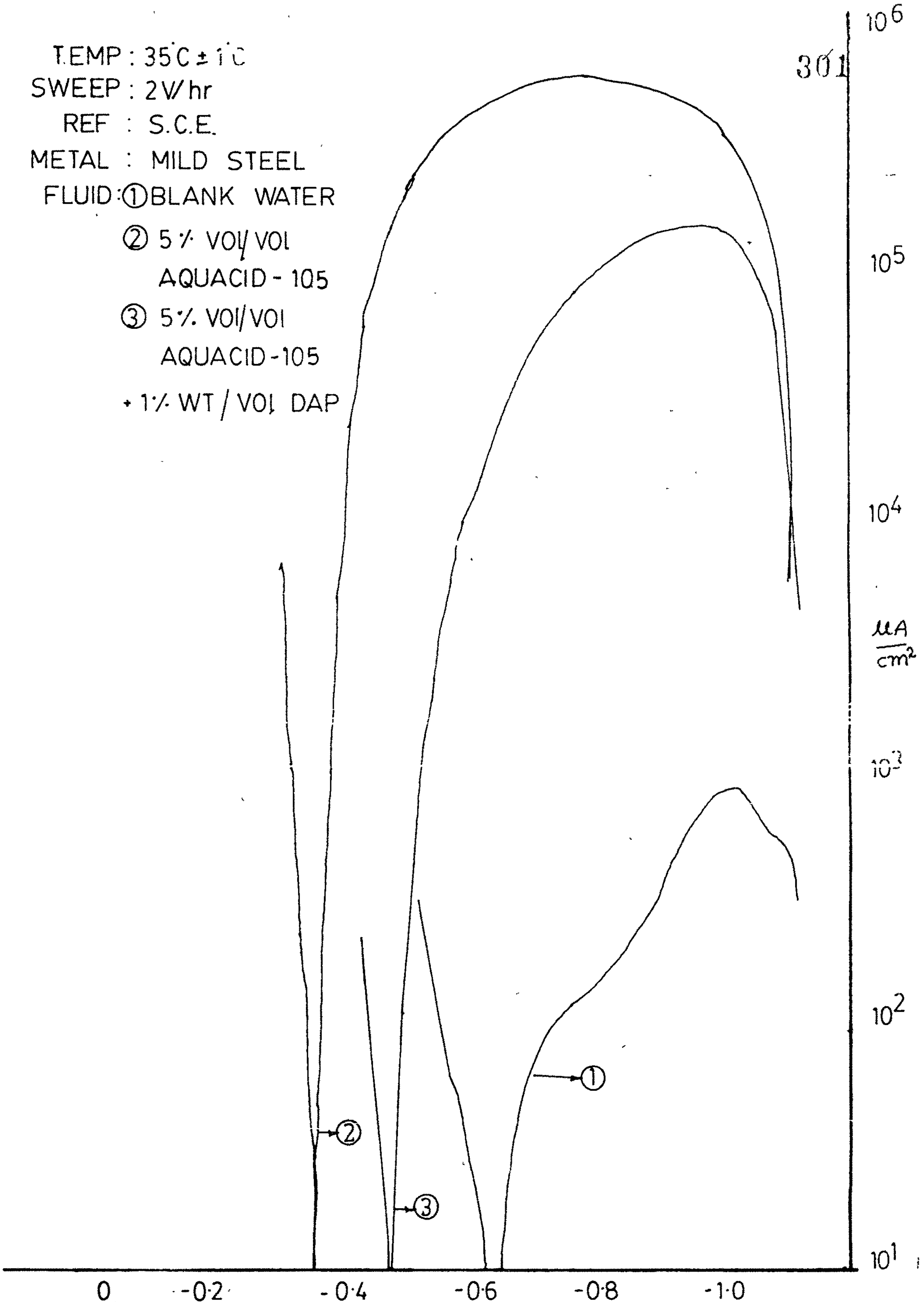

TEMP : 35°C ± 1°C
SWEEP : 2V/hr
REF : S.C.E.
METAL : MILD STEEL
FLUID : ① BLANK WATER
② 5% VOl/VOl AQUACID - 105
③ 5% VOl/VOl AQUACID - 105 + 1% WT/VOl DAP
10^6
10^5
10^4
μA/cm²
10^3
10^2
10^1
①
②
③
0
-0·2
-0·4
-0·6
-0·8
-1·0
POTENTIAL VOLTS VS S.C.E.

FIG.26.

IV. Non heat transfer loop

For evaluating water treatment conditions at plant level non-heat transfer loop with mild steel coupons was placed in inlet, outlet and makeup water by pass line of amonia plant cooling tower and caprolactam plant cooling tower. Flow pattern of cooling water is shown in (fig. 28). The following results were computed:

Scale and corrosion products:

a) Gain or loss during installation g/day
b) Loose scale and corrosion products g/day
c) Tight scale and corrosion products g/day
d) Total scale and corrosion products g/day
e) Actual weight loss of insert g/day
f) Corrosion rate in mils per year

Make-up water:

Make-up water received in various plant of GSFC is from Mahi River. The above results are computed regularly at the gap of month and study was carried out for complete one year. Average monthly analysis of make-up water of ammonia plant and caprolactam is given in Table 66 and Table 67 respectively. On the basis of analysis 99% confidence level of various parameters are given in (Table 110).

Table - 110

Various parameters of Make-up Water (99% confidence level)

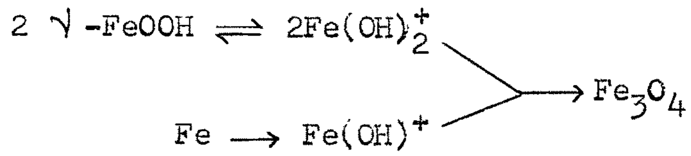
Makeup water	Hardness / chloride	Alkalinity / chloride + sulphate	Corrosion rate MPY
Ammonia Plant	3.02	4.01	7.91
Caprolactam Plant	3.03	4.15	8.07

The corrosion rate of makeup water from ammonia plant and caprolactam plant falls under moderate zone as shown in (fig. 43) and (fig.44). From (fig. 29,30) Langelier index of Makeup water of both plant it is observed that all the 12 samples falls under positive Langelier Index. Positive Langelier index shows scale forming tendency of water so corrosion rate should fall under negligible corrosion zone. The higher corrosion rate in makeup water may be attributed to the fact that $CaCo_3$ may be deposited in non-protective morphology or insufficient carbonate supersaturation to coat the whole system. It is reported that even positive Langelier index may be corrosive if there is presence of aggresive ions (144). Similarly Langelier negative index may be corrosive if it is fairly pure and low in CO_2. Feigenbaun et.al. (145) have reported that in supply water corrosion product $CaCO_3$ present in outer zone while α-FeOOH, $FeCO_3$ and Fe_3O_4 dominate inner zone. The possibility of removal of outerzone by velocity of water all the time which may allow base metal to come in contact with flow of water leads to further corrosion. In makeup water of ammonia plant and caprolactam plant hardness/chloride ratio (Table 110) of 3.02 and 3.03 is obtained instead of desired level of 2.0 and similarly Alkalinity/chloride + sulphate ratio (Table 110) was observed 4.01 and 4.15 respectively instead of desirable ratio of 5.0 to make system free from corrosion (144). The(fig.33) shows akalinity/chloride + sulphate and (fig.31) shows hardness/chloride for 12 samples of makeup water of ammonia plant. The similar data for caprolactam plant makeup water is given in (fig.34) and (Fig.32). The experimental work (146) has demonstrated that the corrosion rate of steel is independent of chloride concentration from very low values to 100 mg Cl^-/l provided the water fontains 100 mg HCO_3^- /l, while in absence of bicarbonate the corrosion rate increases seven fold over the same range of chloride concentration. The hidden factor such as organic matter and some kind of algae and slime forming bacteria can have a masking effect on metallic surfaces and promote differential aeration problems, and certain type of bacteria can themselves become involved in the corrosion process causing significant problems.

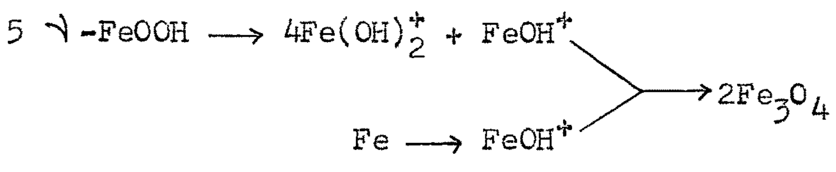
It is reported by Larson and Skold (107) that if pH is around 7 and 8 and epm (chloride + sulphate)/epm (m-alkalinity) is less than 0.1 in make up water than system has relative freedom from corrosion. From table 66 and table 67 it is observed that in majority of cases the makeup water has pH above 8.0 and from table.60 and table-62 it is observed that epm (chloride + sulphate)/epm (M-alkalinity) is above 0.5 in majority of samples, which also support corrosive tendency of makeup water. Regarding scaling mechanism M. Moriwaka and H. Nomura (147) had given some guide line that scaling of total hardness is closely related to that of silica, if total alkalinity is low, the deposition of magnesium silicate occur. High total alkalinity of makeup water accelerate scaling of calcium and silica may act as a catalyst for deposition of calcium carbonate. Scale aboundant in silica cause less trouble, while calcium reach scales deteriorate heat exchanger performance. Deposition of calcium carbonate does not occur at positive Langelier index if total alkalinity is due to synergism of hardness and silica. In high calcium hardness and total alkalinity water calcium carbonate deposition occurs in accordance with Langelier's expression.

The corrosion rate of makeup water observed by non-heat transfer loop method was found high compare to static condition. For practical purpose make up water collected shows corrosion rate under static condition after 30 days as 3.75 MPY (Table 37) and analysis is given in Table 22. Now the make up water corrosion rate by non-heat transfer loop method (i.e. under velocity) of ammonia plant and caprolactam plant on 99% confidence level is 7.91 and 8.07 respectively (table 110). The higher corrosion rate in non-heat transfer loop method is attributed to velocity. Due to velocity whatever protective layer is formed is disturbed all the time and base metal is exposed to fresh water enriched with dissolved oxygen.

Regarding corrosion products in supply water Graham (148) has reported $\gamma\text{-Fe}_2\text{O}_3$, Fe_3O_4 and $\alpha\text{-FeOOH}$ as major corrosion products. Lepidocrocite has been reported to be a dominant compound present in mild steel. Corrosion products, with α-FeOOH and α-Fe_2O_3 existing in small amounts (149). Regarding corrosion product another possibility is that of γ-FeOH, formed initially being transformed to Fe_3O_4 by one of the two likely mechanisms proposed by Smith and McEnamey (150). The first pathway is a dissolution - precipitation reaction in which γ-FeOOH dissociate into $Fe(OH)_2^+$ ions which in turn reacts with $FeOH^+$ ions to precipitate as Fe_3O_4.



The second mechanism involves reductive dissolution in which γ-FeOOH is dissolved with partial reduction to give both $Fe(OH)^+$ and $Fe(OH)_2^+$ ions which react to yield magnetite.



While comparing all the three systems i.e. inlet, outlet and makeup water of ammonia and caprolactam plant, it is observed that in both the cases corrosion rate of inlet system is high compare to outlet and makeup water. The 99% confidence level of corrosion rate is given in table 111.

Table - 111

99% confidence level of corrosion rate in MPY

Plant	Makeup water	Inlet	Outlet
Ammonia Plant	7.91	10.59	5.42
Caprolactam Plant	8.07	14.01	5.14

The higher corrosion rate in inlet system compare to outlet and makeup water is due to high temperature and process contamination. The main effects of increase in temperature are (i) it increases the rate of chemical reaction (ii) it lessness the solubility of gases in water (iii) it may affect the solubility of the possible products of corrosion reaction and (iv) decrease viscosity.

The raise in temperature may soften bicarbonate hardness and release some CO_2 which accelerates corrosion.

It is observed from table 64 and 65 that in ammonia plant and caprolactam plant cooling water corrosion has some relation with total scale and corrosion products. With increase in total scale and corrosion products increase in corrosion rate was observed in makeup, inlet and outlet water. The graphical representation of total scale and corrosion products g/day for ammonia plant and caprolactam plant is given in (fig.47) and (fig.48) respectively. In the similar manner it is observed that in majority of cases with increase in loose scale and corrosion products shows increase in corrosion rate of inlet, outlet and makeup water. This may be due to fact that increase of corrosion product which leads to dissolution of base metal by flowing water.

From (fig.39,40) and (fig.37,38) it is noticed that pH and alkalinity of makeup water is high compare to outlet water in ammonia plant and caprolactam plant, eventhough corrosion rate of makeup water is high compare to outlet water as shown in (fig.43) and (fig.44). Similarly Langelier index was found positive in makeup water of ammonia plant (fig.29) and caprolactam plant makeup water (fig.30) compare to langelier index of outlet cooling water of ammonia plant (fig.41) and caprolactam plant cooling water (fig.42). It is also observed from (fig. 35) that hardness of makeup water is low compare to outlet cooling water of ammonia plant. Similarly in caprolactam plant hardness of makeup water is low compare to outlet cooling water which is shown in (fig.36). This leads us to think that instead of alkalinity and pH, hardness is playing an important role in curtailing corrosion rate. So for predicting scaling and corrosive tendency require some modification and some more factors should be taken in account. COX and Roetheli (151) as well as Lee (152) found that increasing the oxygen concentration of water leads to faster corrosion of steel. Stum (153) evaluated corrosivity of several waters whose saturation indexes varied from -2.5 to +0.4. When this corrosion data was analysed there was poor correlation between saturation index and corrosion rate for coupons placed in service line after 5, 20 and 50 days. The predictive equation (154) describing eight variable model suggests that increasing chloride, sulfate, alkalinity and dissolve oxygen would accelerate corrosion, where as increase in calcium, buffer capacity, saturation index and exposure time lower the corrosion rate. Alkalinity was found accelerating factor instead of inhibitive parameters as has been observed in some corrosion studies (155). This could be due to masking effect rendered by increasing conductivity which subsequently increased the ionic strength. In other words, there could be a point reached when the inhibitive influence of alkalinity could be overwhelmed by the ionic conductivity which favours corrosion.

From below (table 112) it is clear that hardness is the inhibiting factor for corrosion rate. In ammonia plant cooling water outlet 99% confidence level of hardness is 229.65 ppm and in caprolactam plant cooling water outlet having hardness is 397.04 ppm and corrosion rate is 5.42 and 5.14 mpy respectively. Similarly alkalinity is high in ammonia plant cooling water outlet compare to caprolactam plant cooling water which is accelerating factor.

Table 112

99% Confidence level cooling water outlet

Plant	Hardness ppm	Alkalinity ppm	Corrosion rate mpy
Ammonia	229.65	65.58	5.42
Caprolactam	397.04	63.75	5.14

Similarly as discussed earlier in makeup water that velocity plays an important role in increasing corrosion rate is true in the case of outlet water of caprolactam plant and ammonia plant, the same water is also remain enriched with dissolve oxygen. The ammonia plant and caprolactam plant cooling water was taken for inhibitor evaluation study, experiment under static condition shows blank water corrosion rate in ammonia plant after 30 days exposure as 2.77 mpy (Table 33), compare to 5.42 MPY corrosion rate under velocity. Similarly for caprolactam plant 2.76 MPY (Table 34), compare to 5.14 MPY under velocity. The analysis of ammonia plant and caprolactam plant cooling water is given in (table 18) and (table 19) respectively.

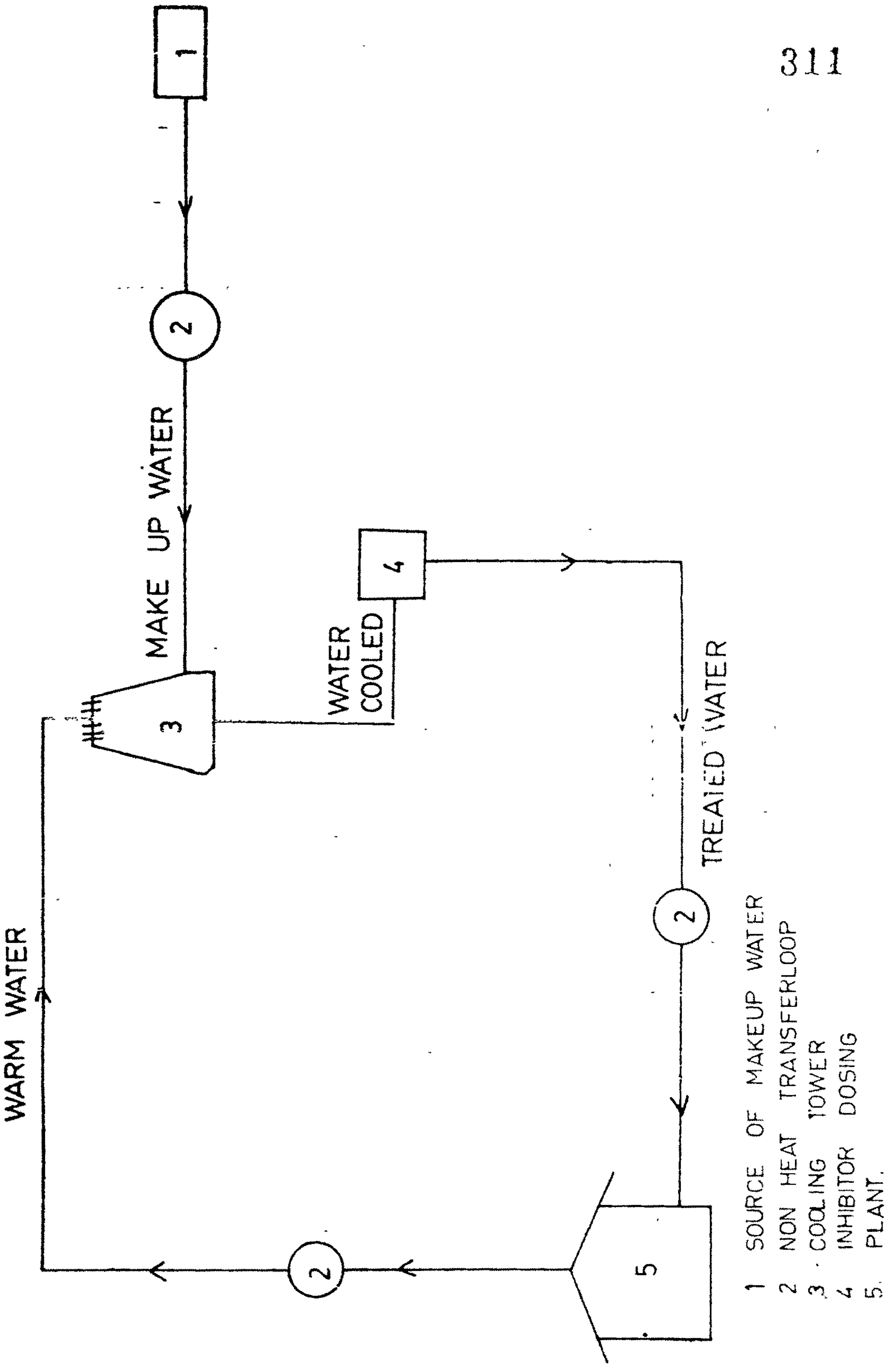


FIG. 28 FLOW PATTERN OF COOLING WATER.

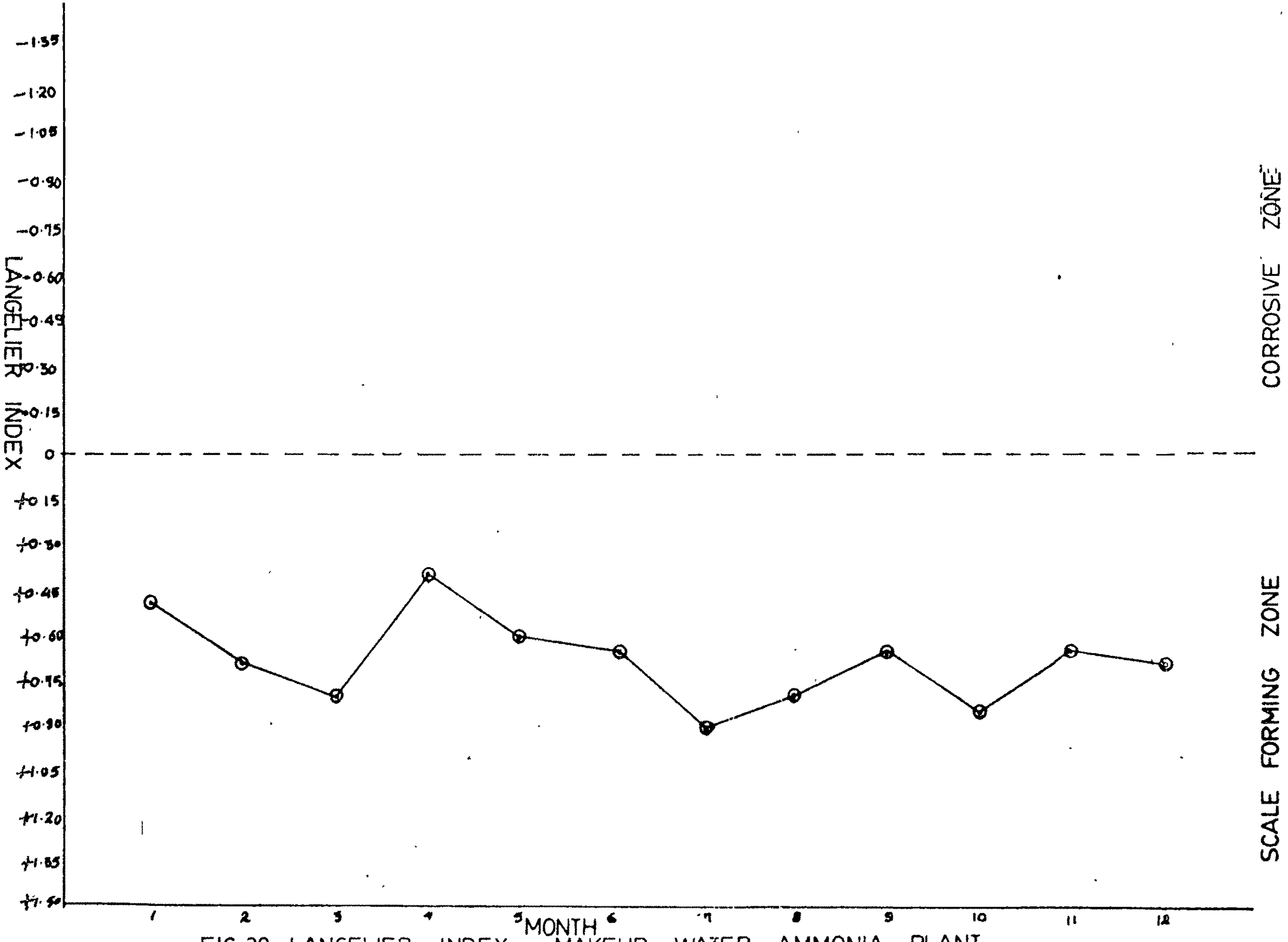


FIG.29 LANGELIER INDEX MAKEUP WATER AMMONIA PLANT

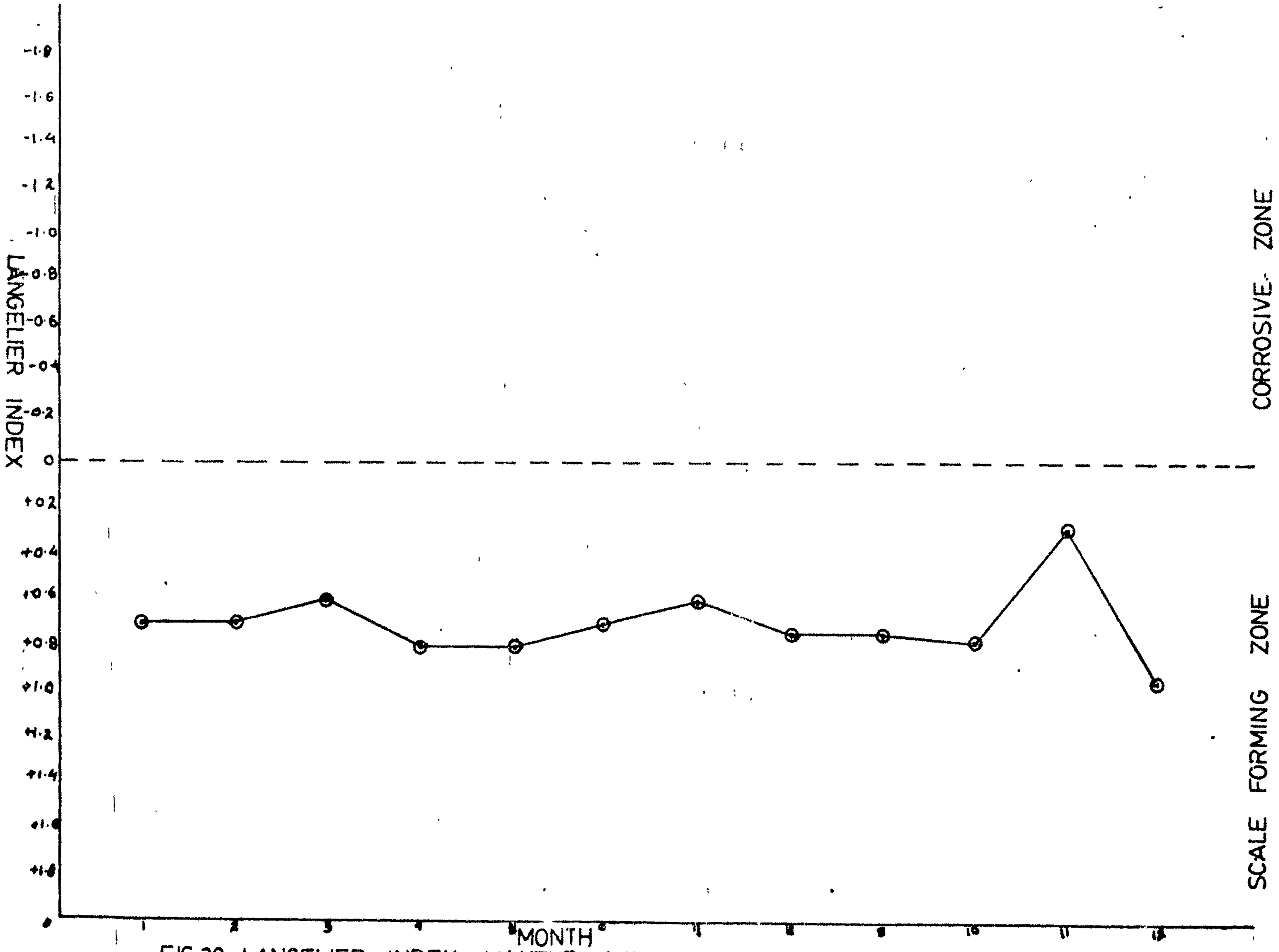


FIG.30. LANGELIER INDEX MAKEUP WATER CAPROLACTAM PLANT.

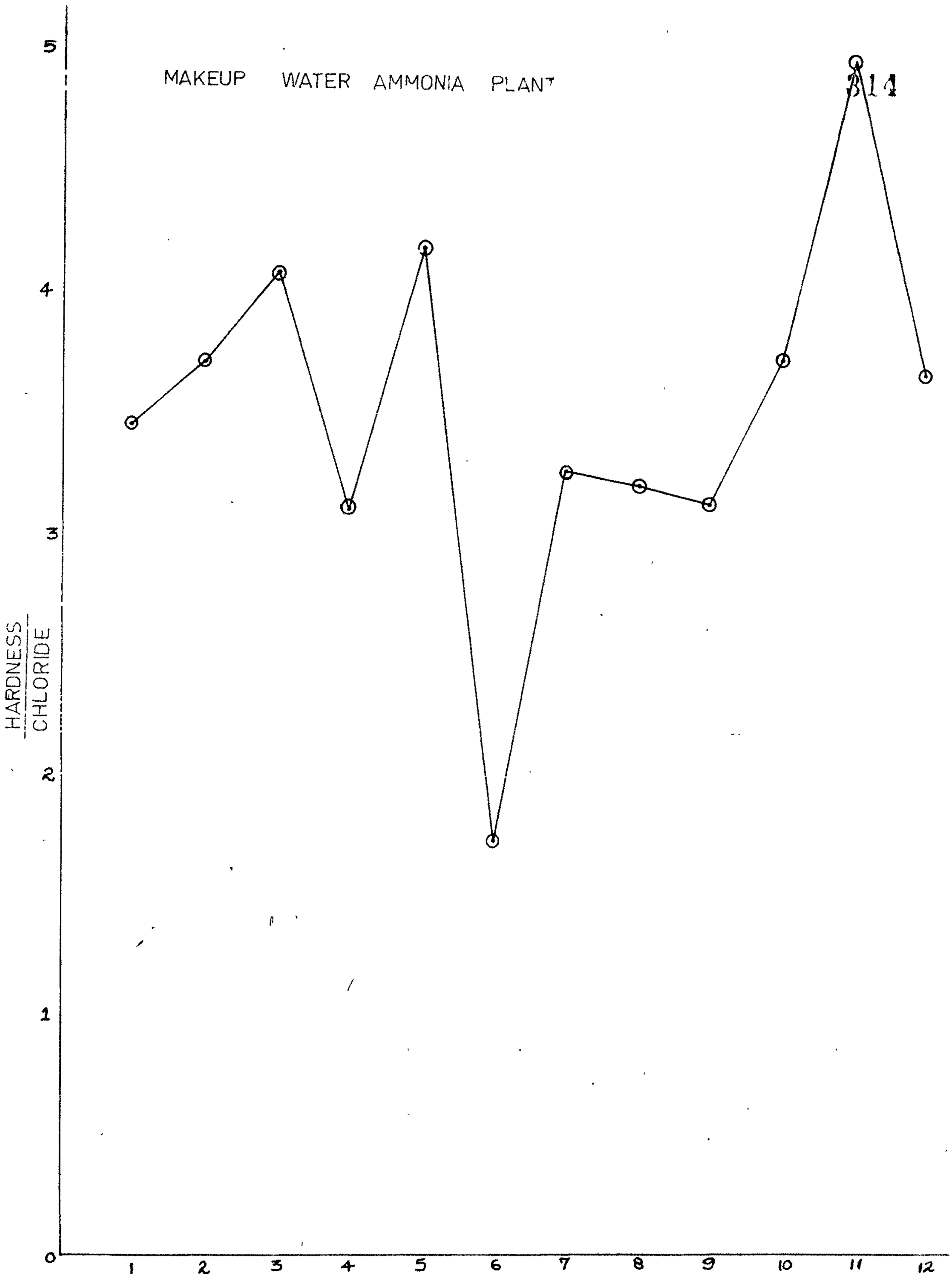


FIG. 31 HARDNESS/CHLORIDE MAKEUP WATER AMMONIA PLANT

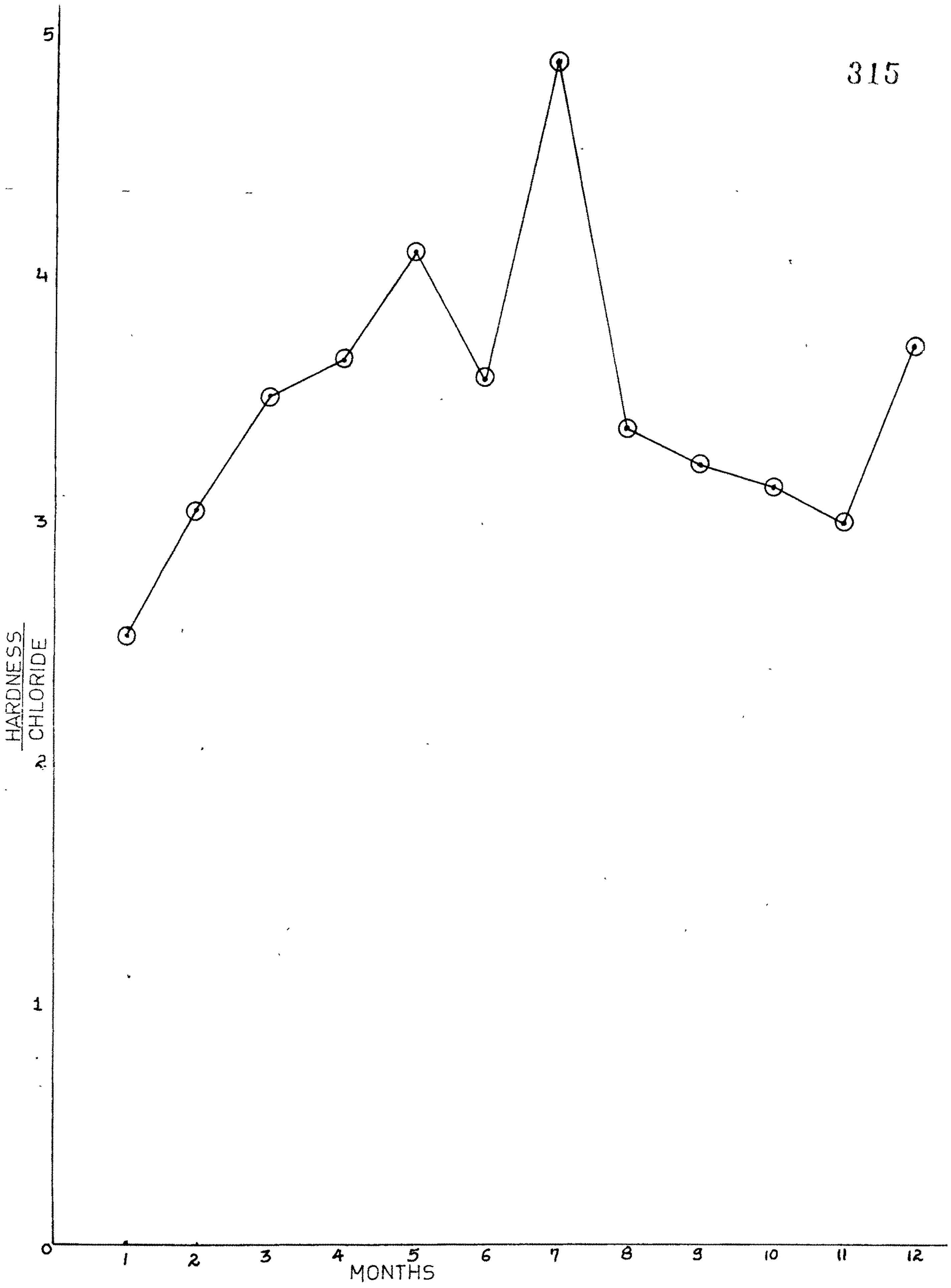


FIG. 32 HARDNESS/CHLORIDE MAKEUP WATER CAPROLACTAM PLANT

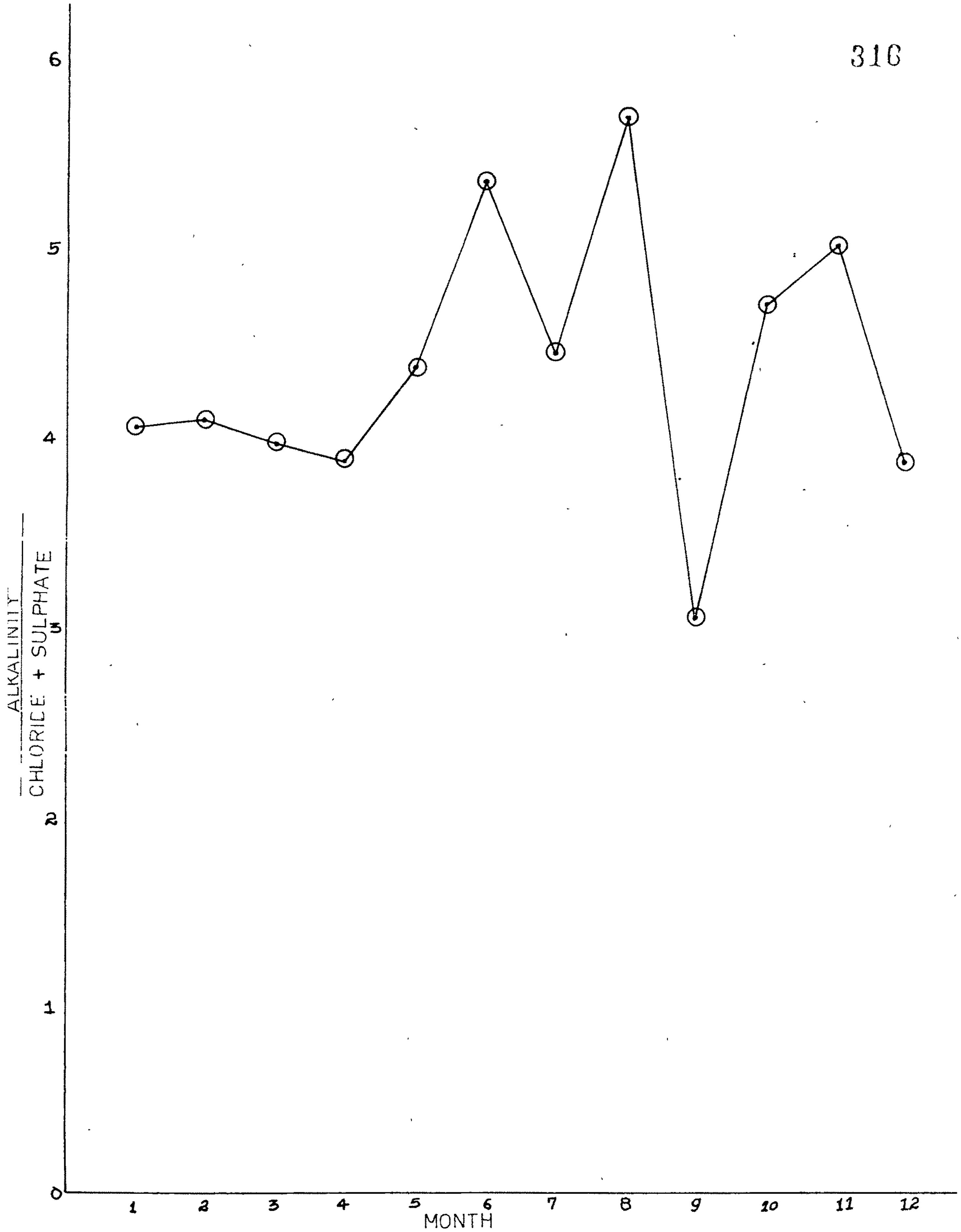


FIG. 33-ALKALINITY / CHLORIDE + SULPHATE MAKEUP WATER AMMONIA PLANT

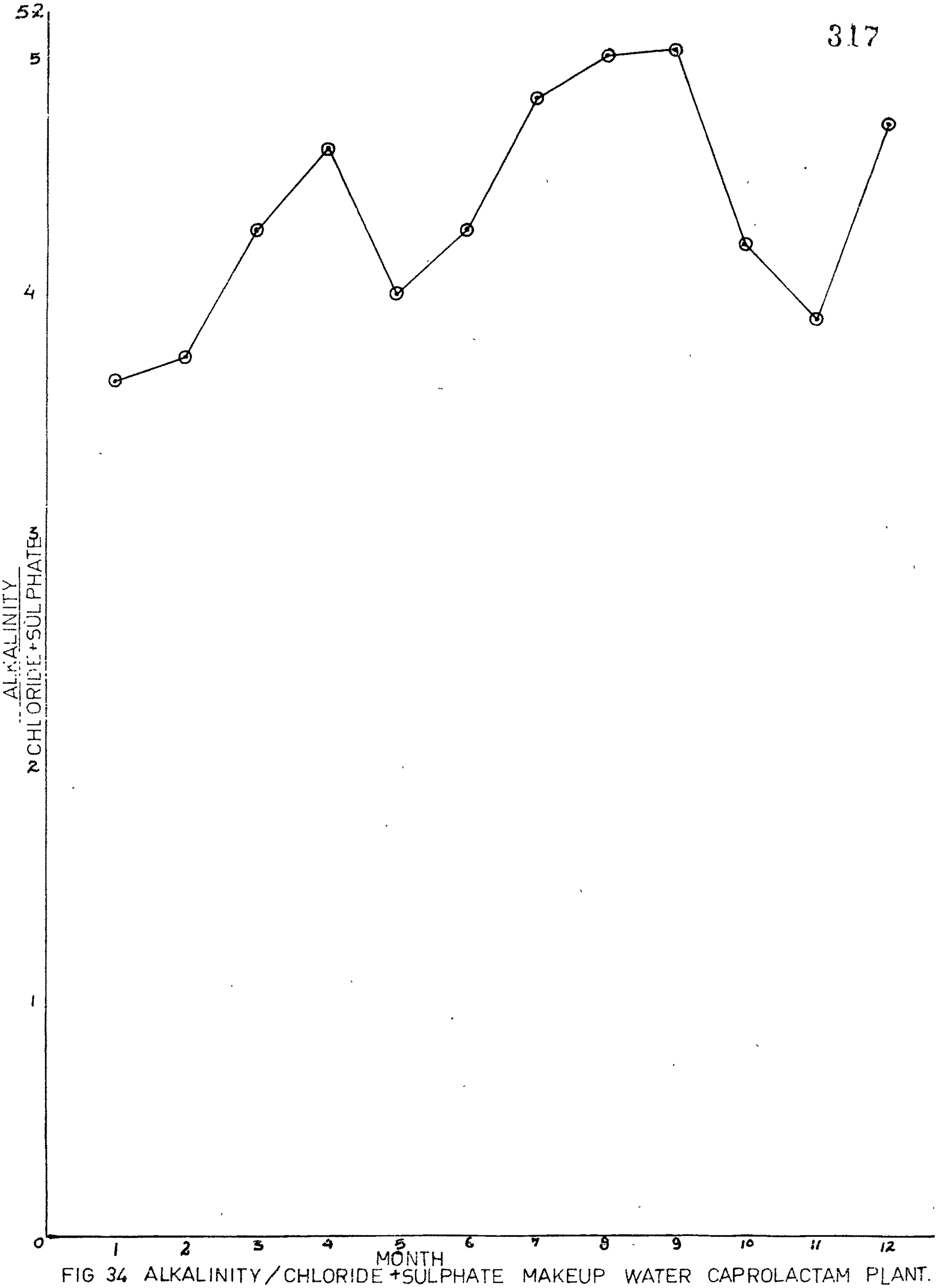


FIG 34 ALKALINITY / CHLORIDE + SULPHATE MAKEUP WATER CAPROLACTAM PLANT.

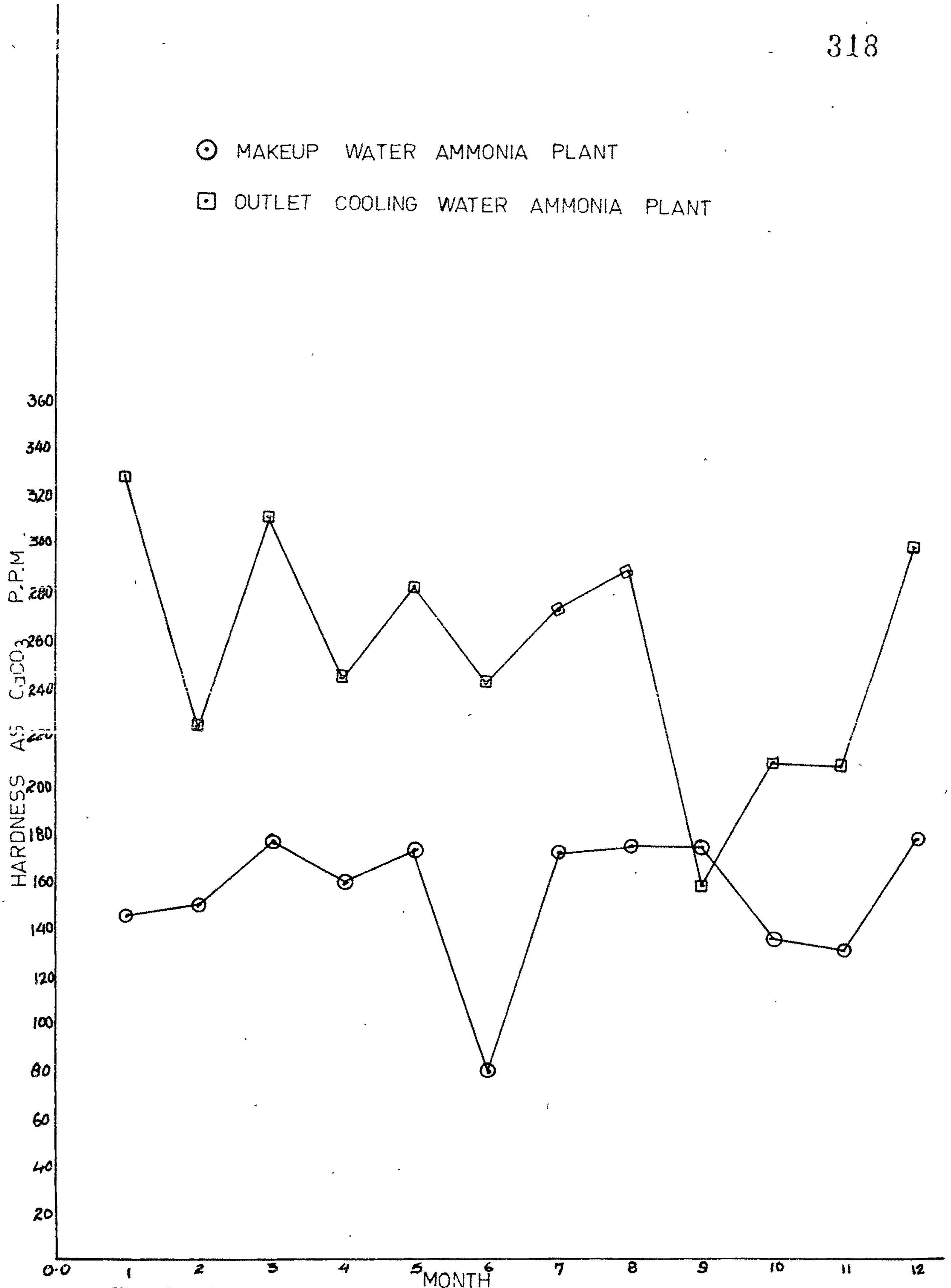


FIG 35 HARDNESS IN PPM MAKEUP WATER AND OUTLET COOLING WATER OF AMMONIA PLANT

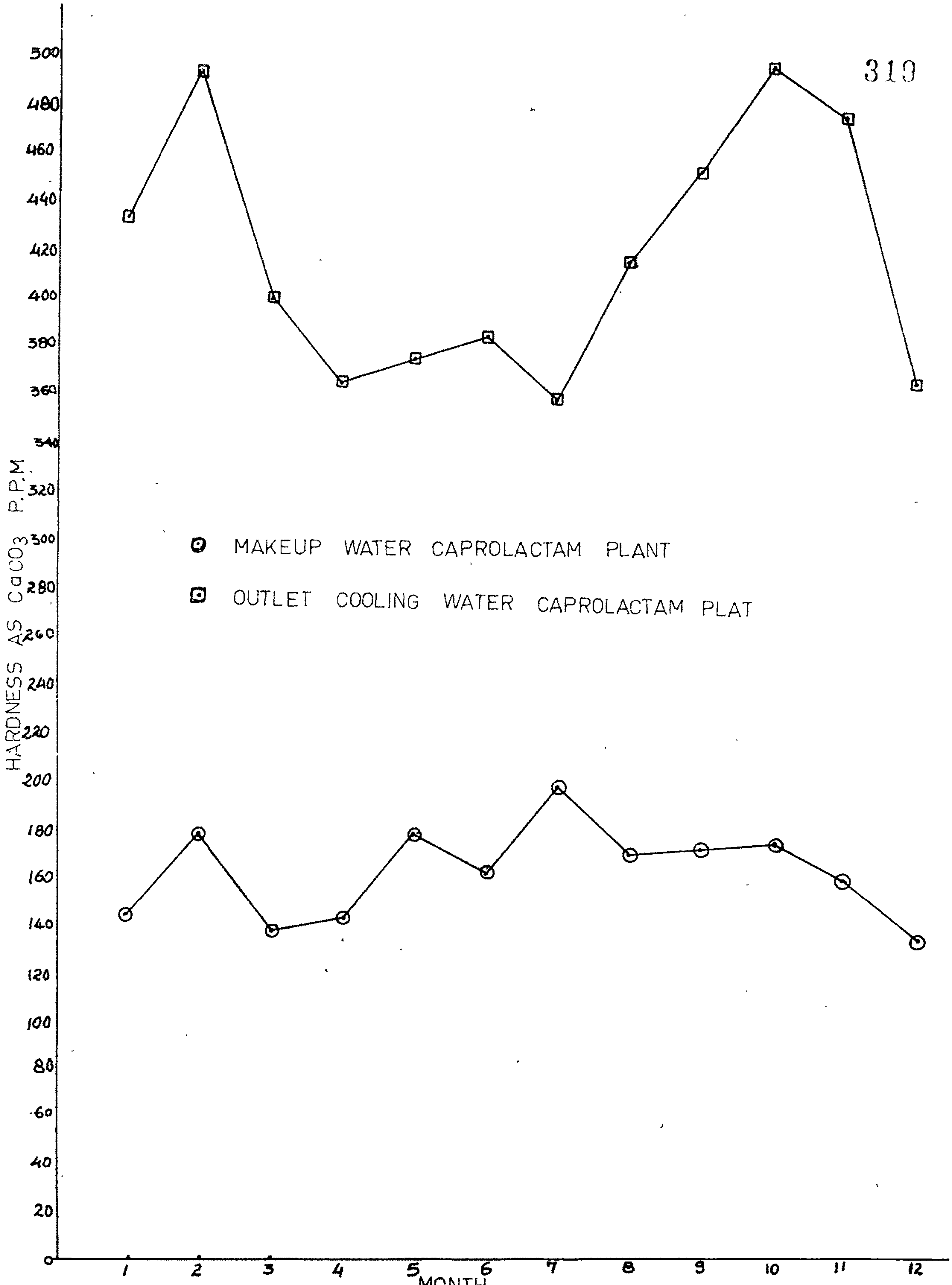


FIG 36 HARDNESS IN P.P.M MAKEUP WATER AND OUTLET COOLING WATER OF CAPROLACTAM PLANT

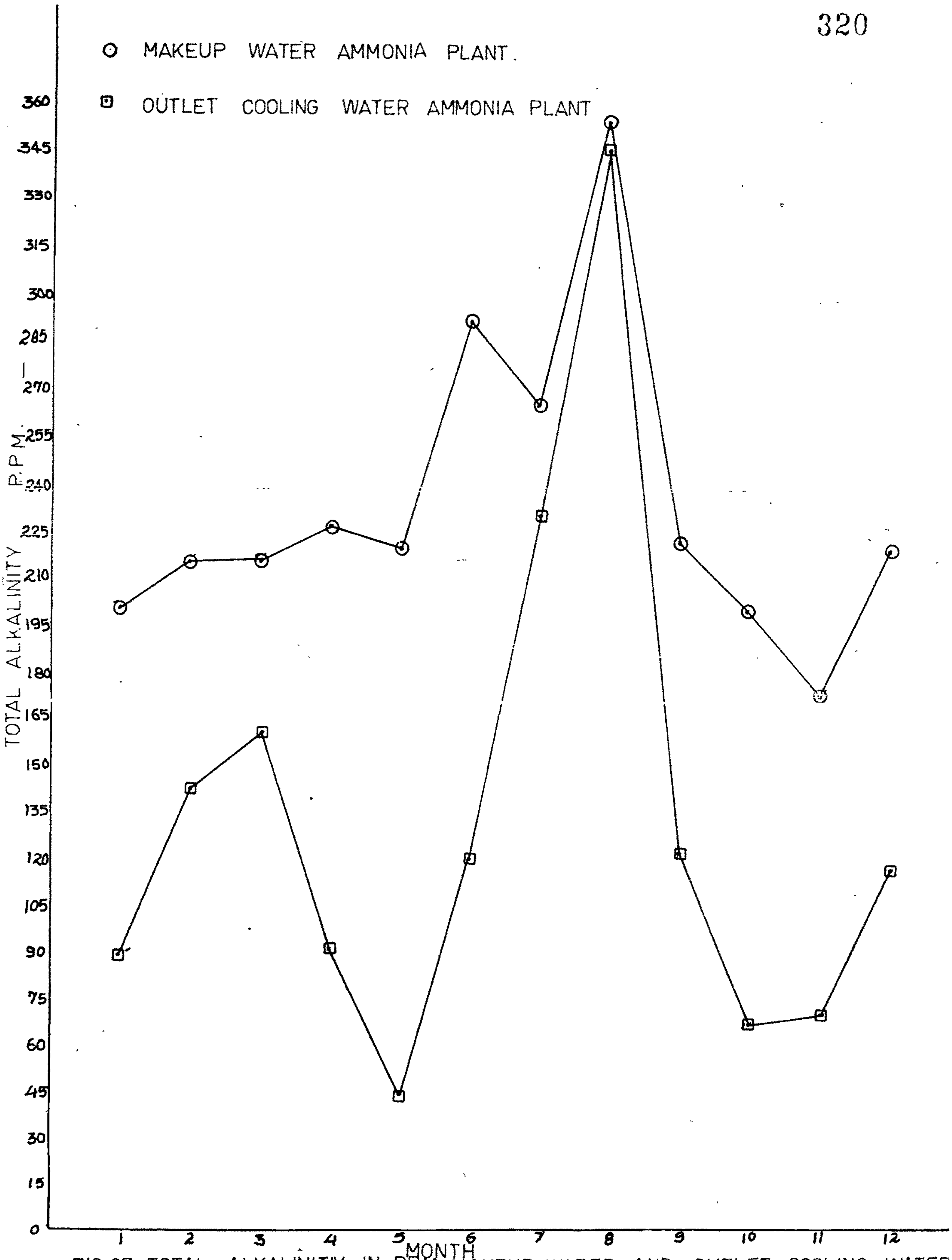


FIG 37 TOTAL ALKALINITIY IN PPM MAKEUP WATER AND OUTLET COOLING WATER OF AMMONIA PLANT

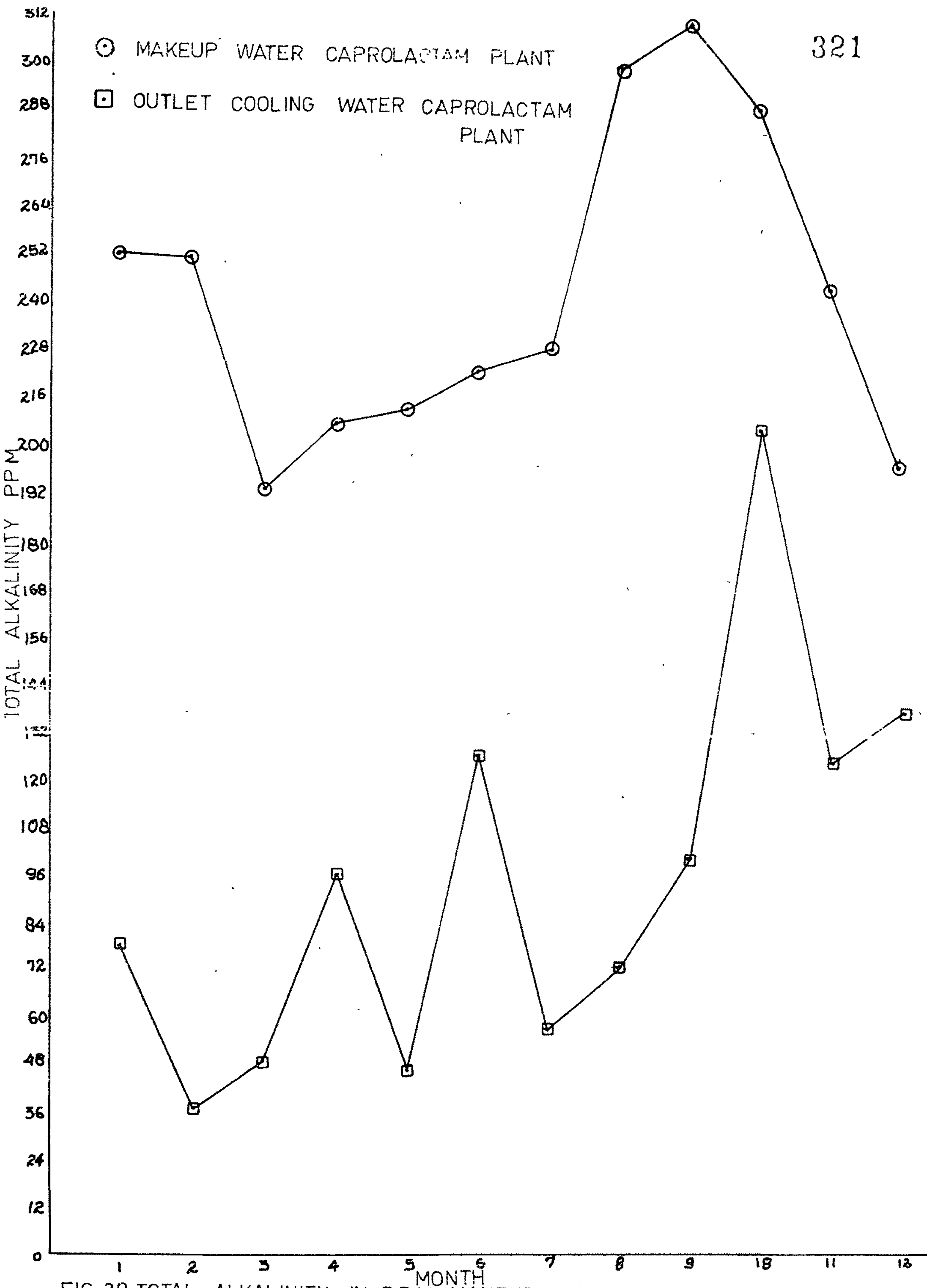


FIG 38 TOTAL ALKALINITY IN PPM MAKEUP WATER AND OUTLET COOLING WATER OF CAPROLACTAM PLANT

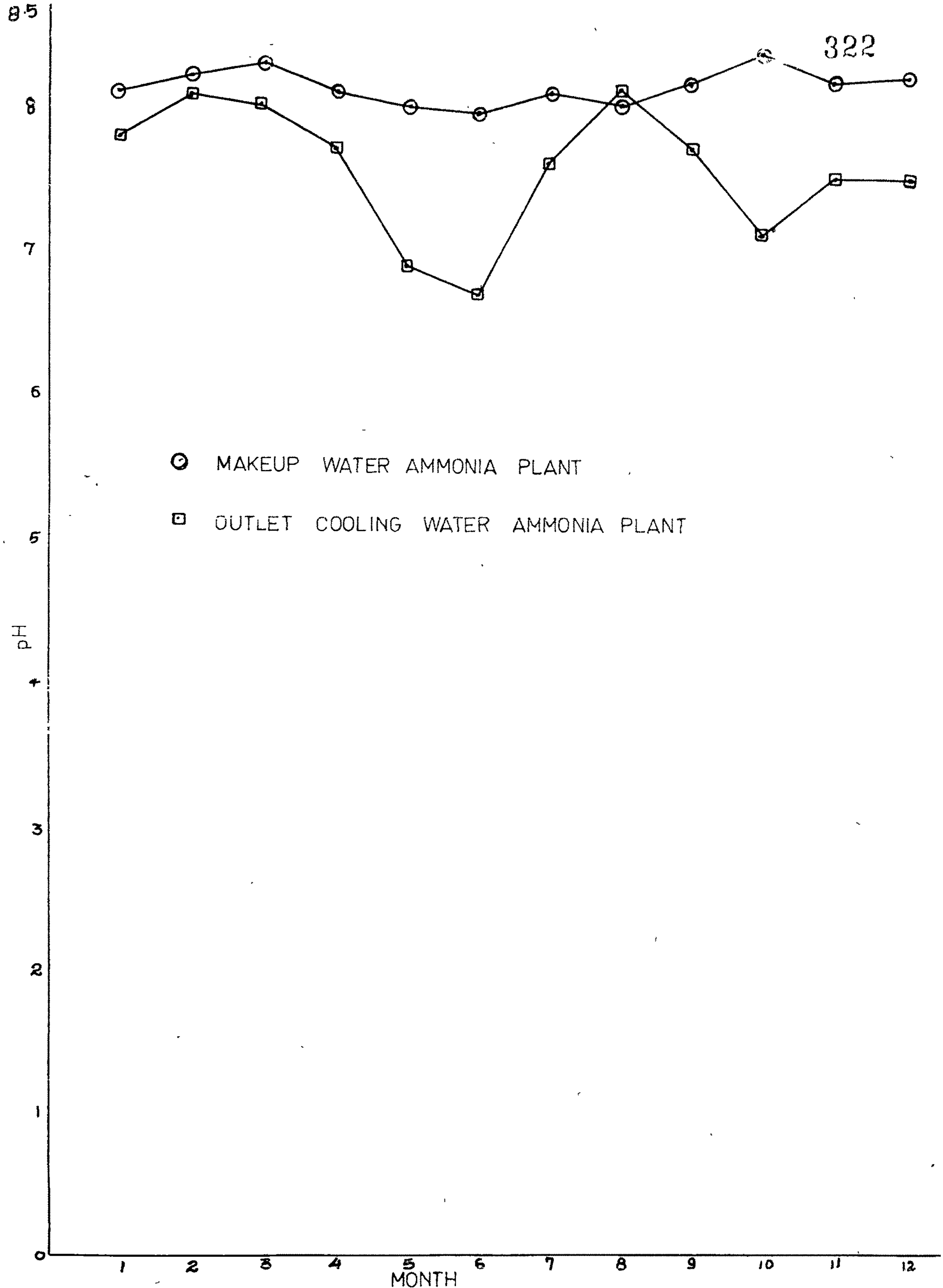


FIG 39 pH MAKEUP WATER AND OUTLET COOLING WATER OF AMMONIA PLANT

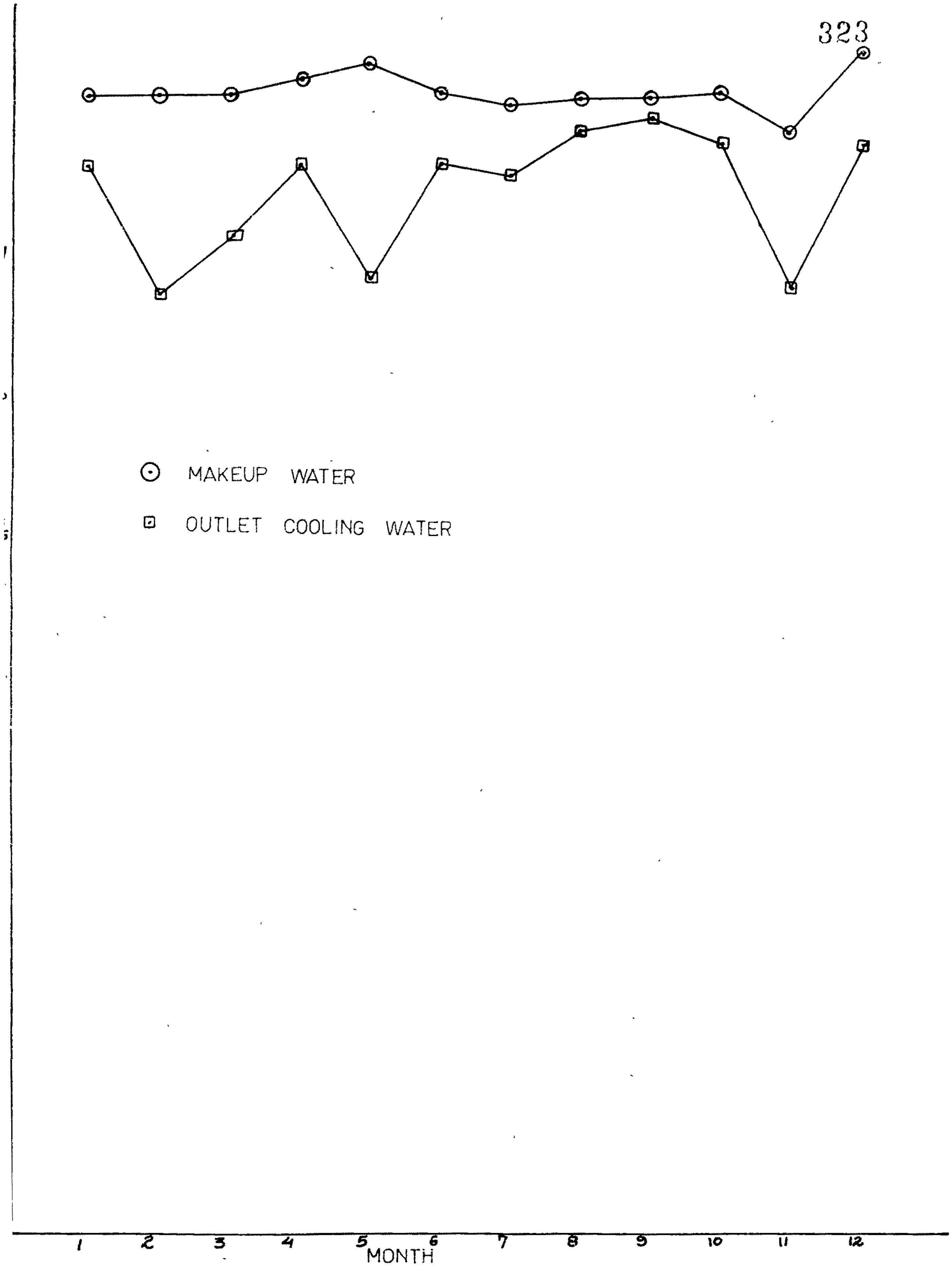


FIG.40 pH MAKEUP WATER AND OUTLET COOLING WATER OF CAPROLACTAM PLANT

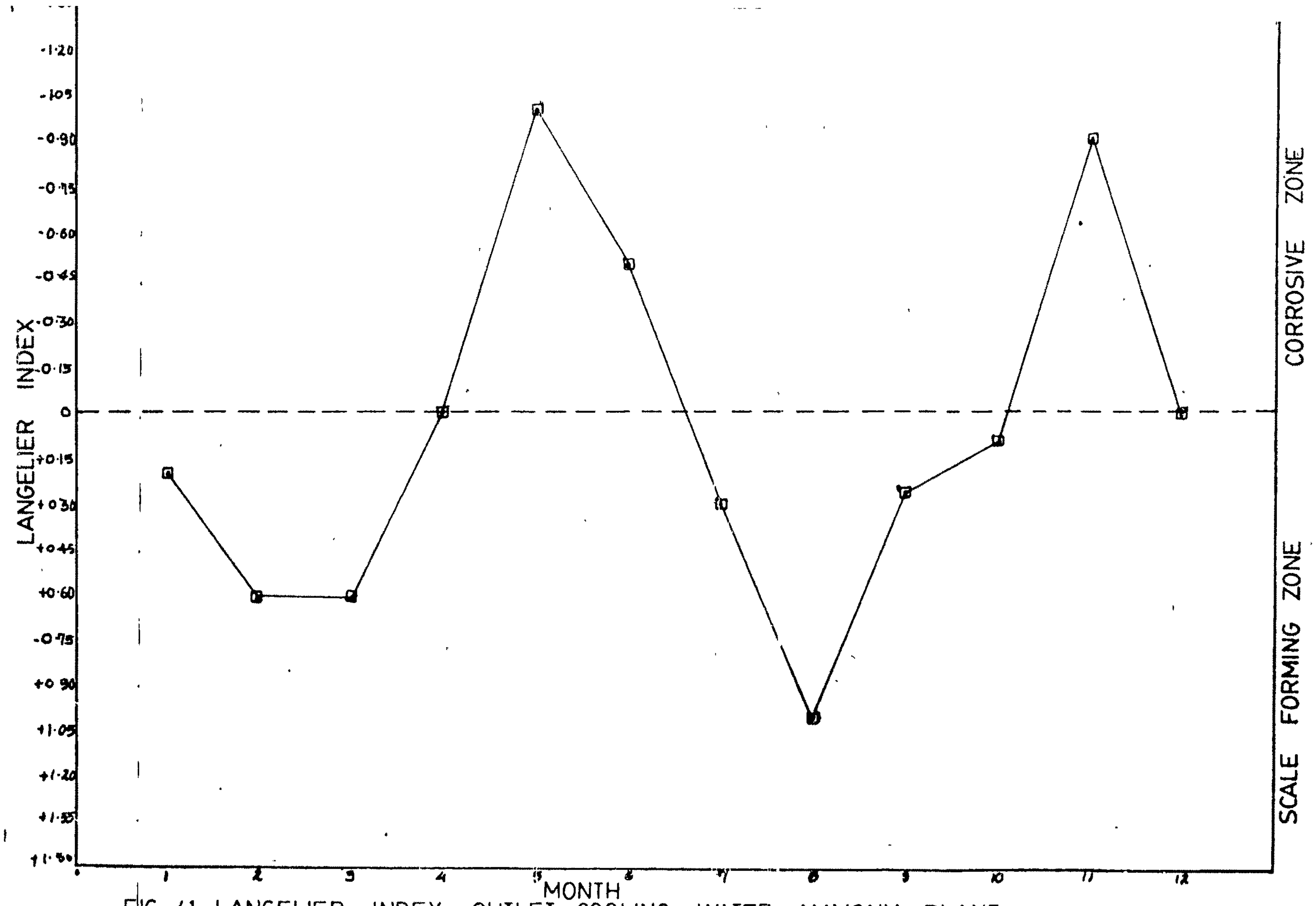


FIG 41 LANGELIER INDEX OUTLET COOLING WATER AMMONIA PLANT.

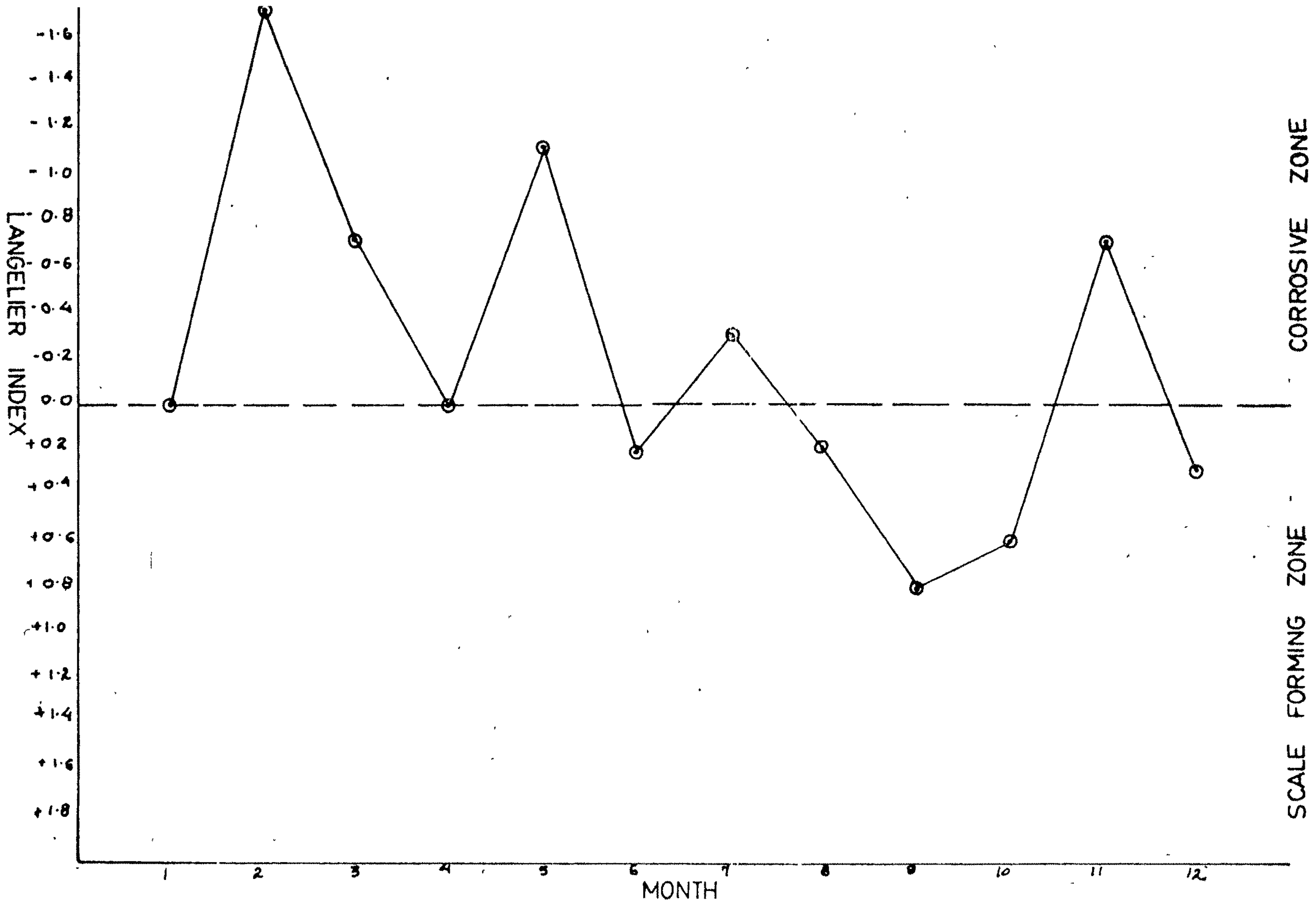


FIG.42 LANGELIER INDEX - OUTLET COOLING WATER CAPROLACTAM PLANT.

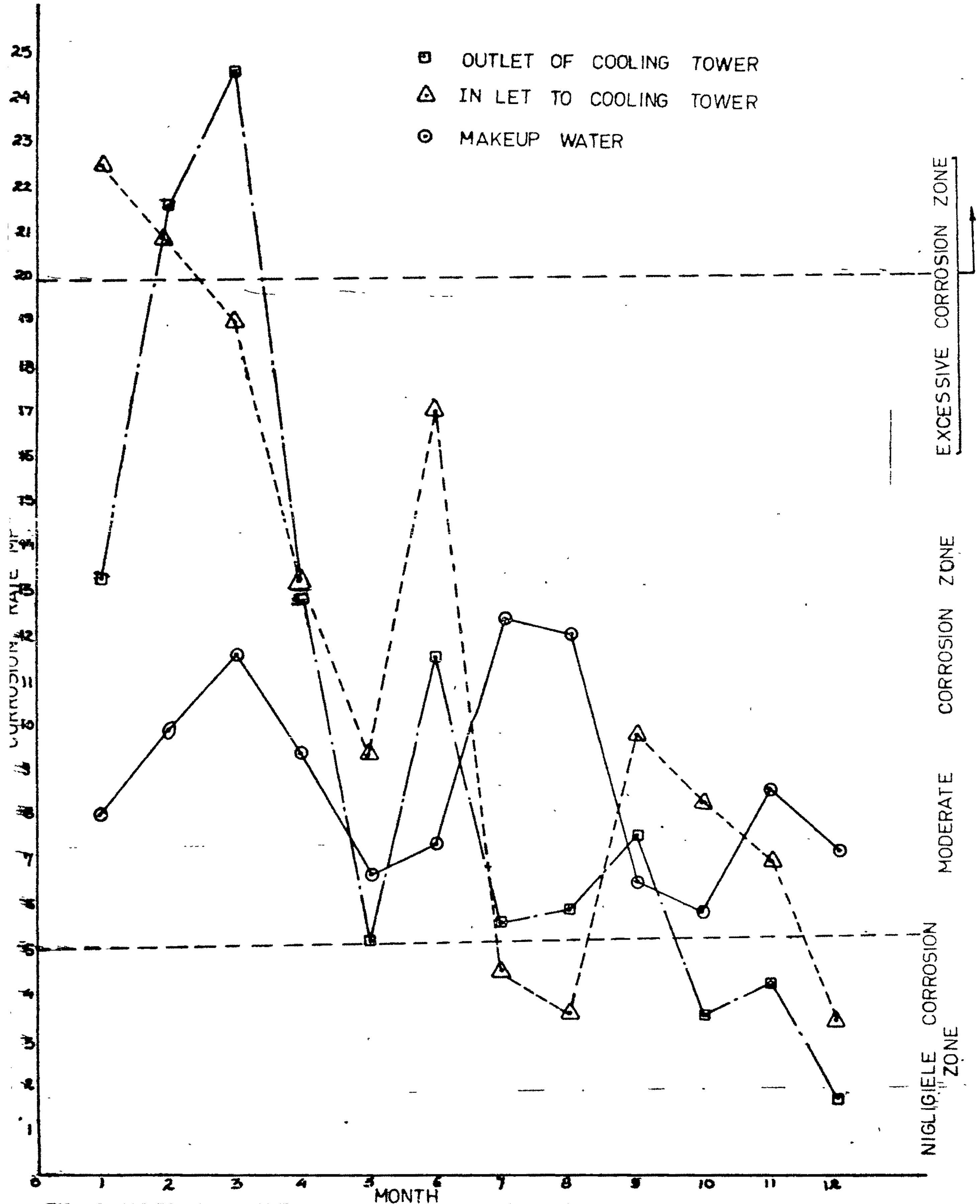


FIG 43 CORROSION RATE IN MPY COOLING WATER AMMONIA PLANT

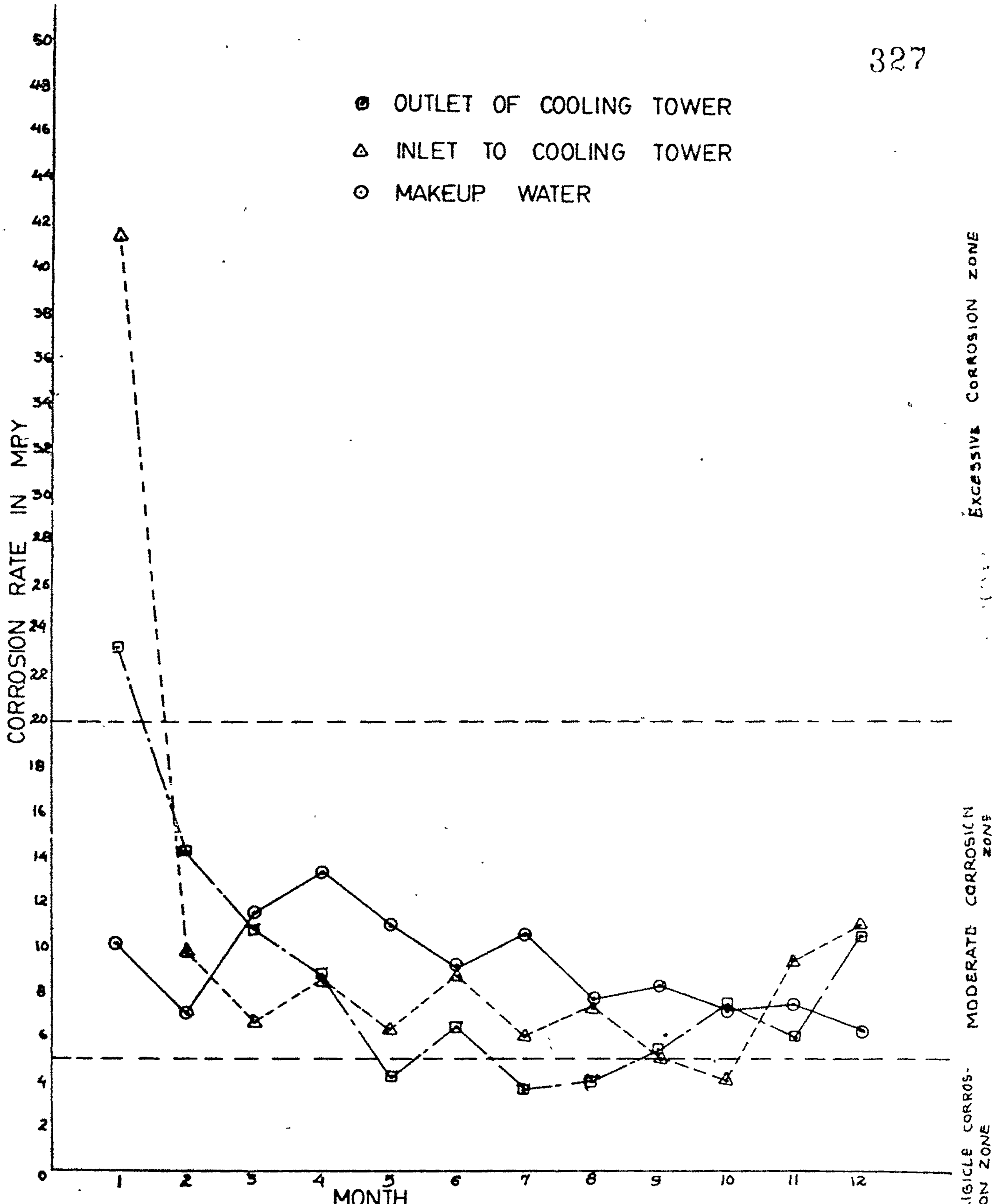


FIG. 44 CORROSION RATE IN MPY COOLING WATER CAPROLACTM PLANT.

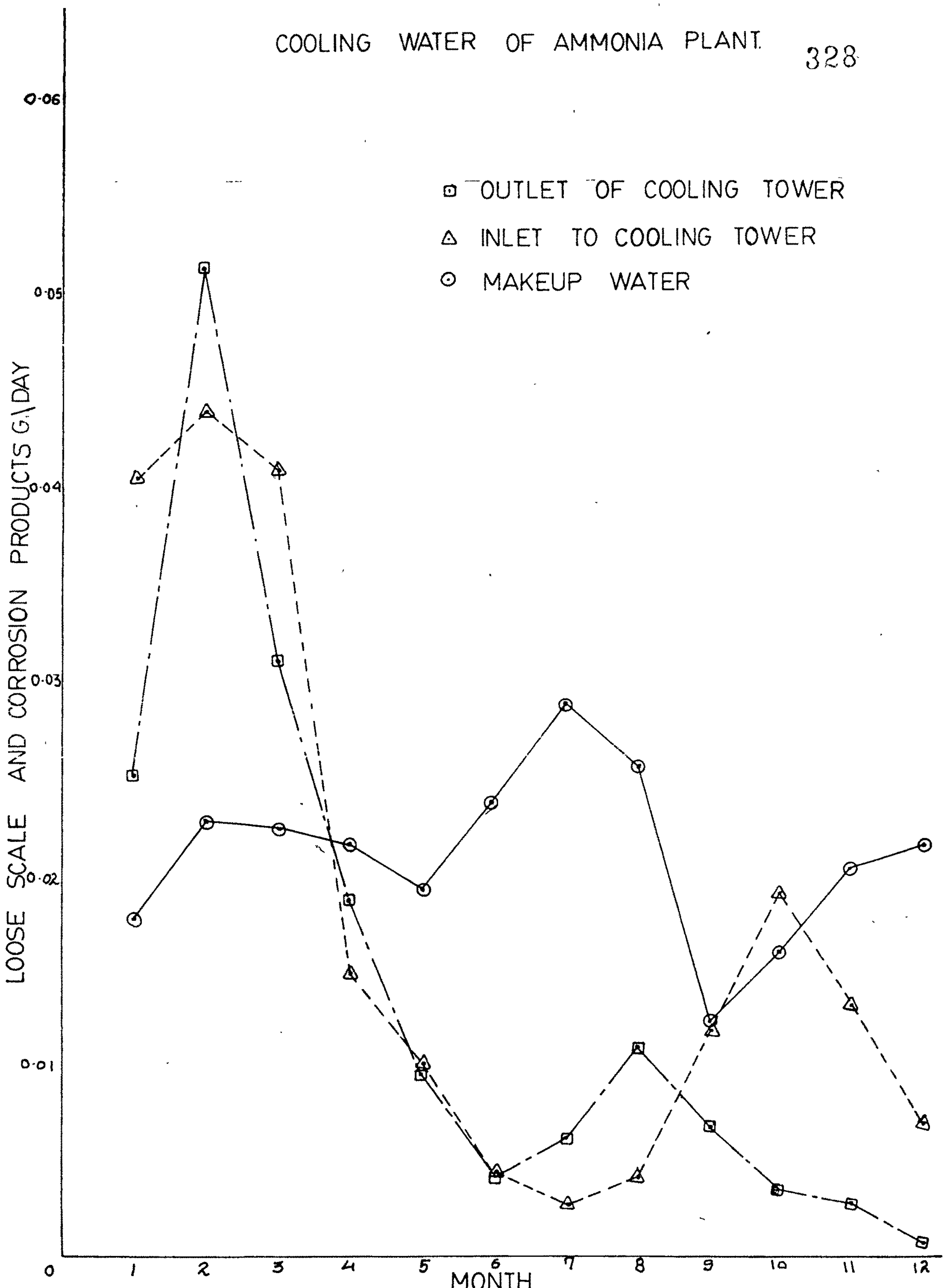


FIG.45 LOOSE SCALE AND CORROSION PRODUCTS G\DAY - COOLING WATER AMMONIA PLANT

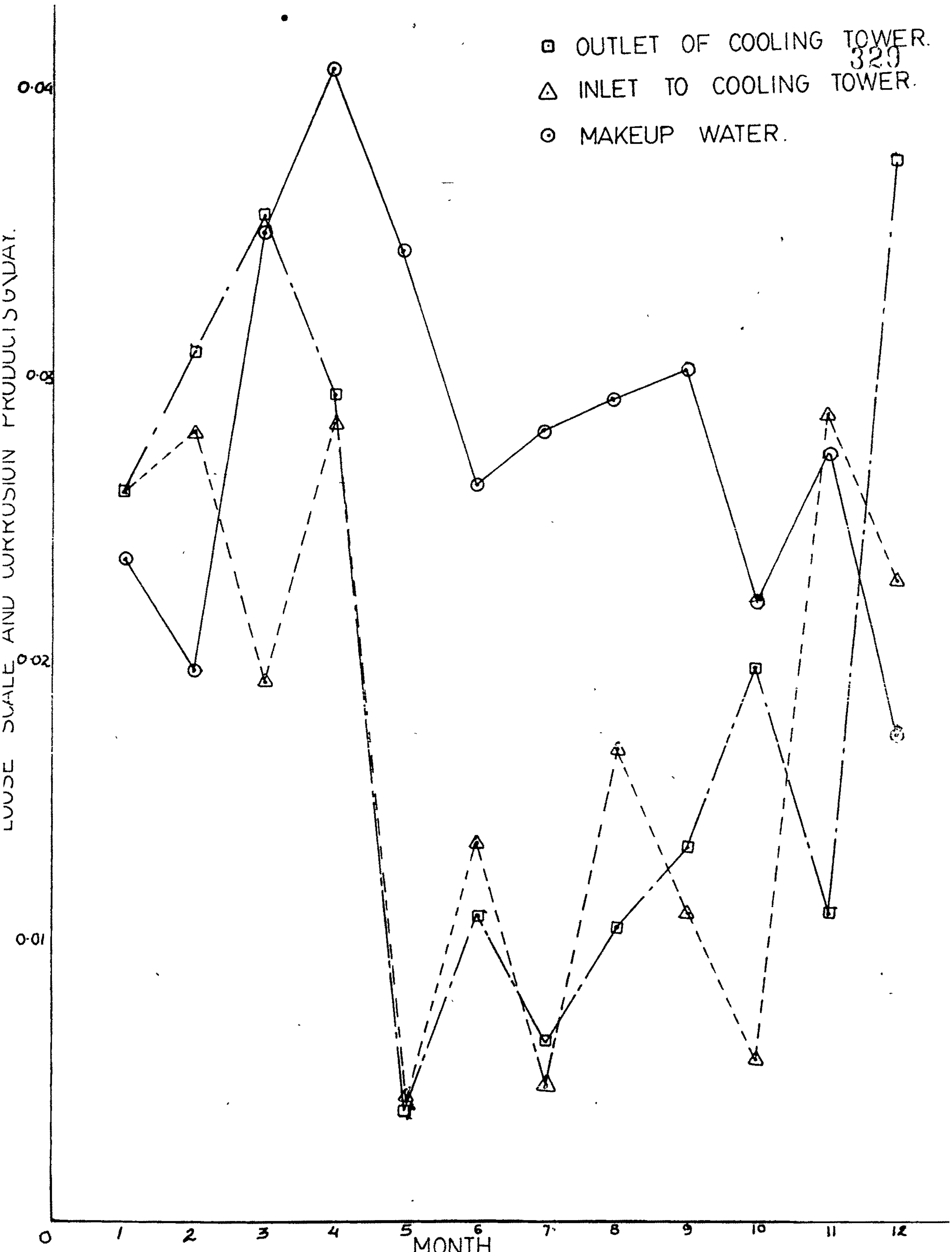


FIG.46 LOOSE SCALE AND CORROSION PRODUCTS G\DAY - COOLING WATER CAPROLACTAM PLANT.

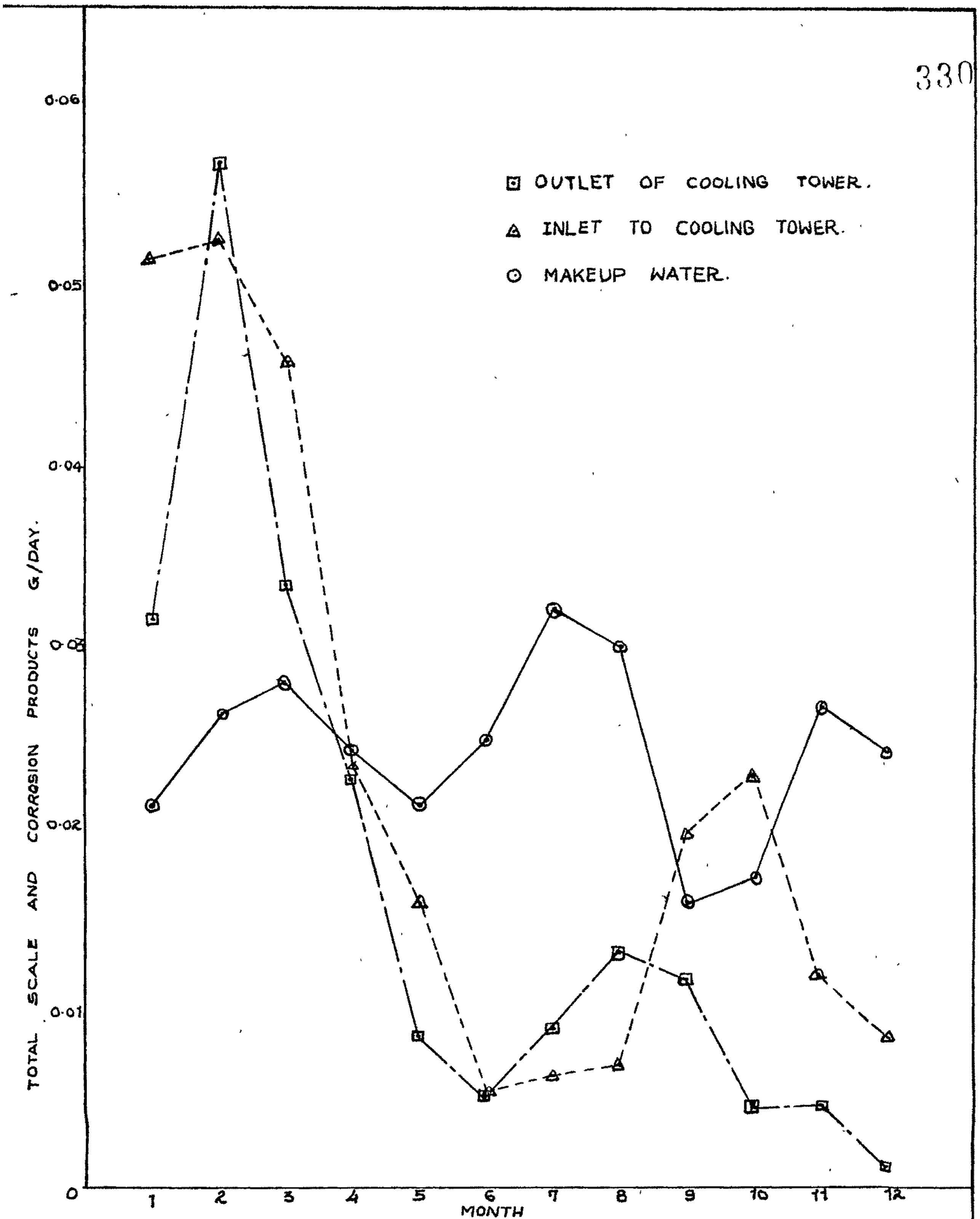


FIG. 47 TOTAL SCALE AND CORROSION PRODUCTS G/DAY - COOLING WATER AMMONIA PLANT.

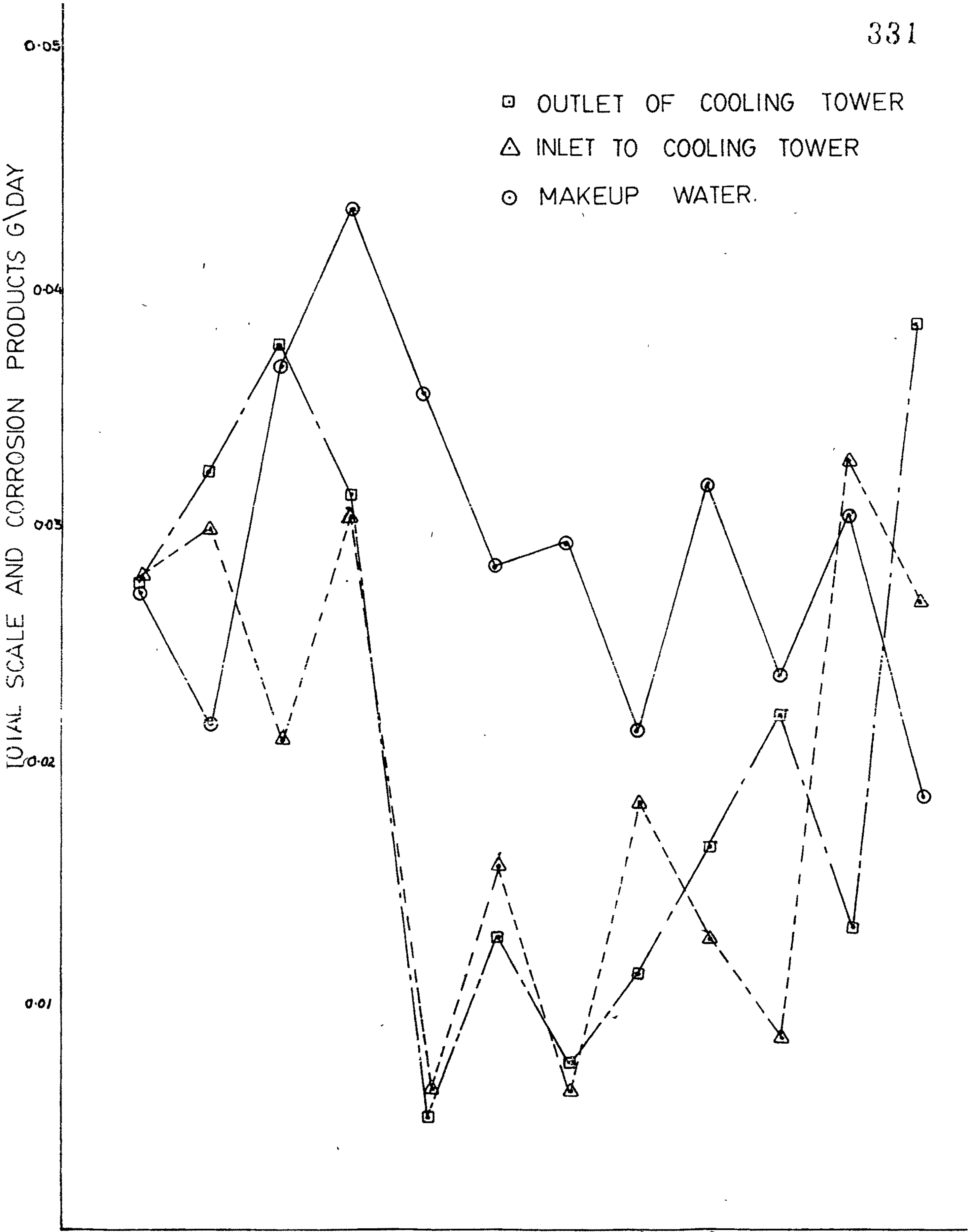


FIG 48 TOTAL SCALE AND CORROSION PRODUCTS G\DAY - COOLING WATER CAPROLACTAM PLANT.