A. von KOEPPEN, A.F. PASOWICZ, and B. A. METZ,
Wright Chemical Corp.

24184
PDF

~~FHP0215~~

Non-Chromate Corrosion Inhibitors

Different types of nitrogen-containing, organic non-chromate corrosion inhibitors were developed that provide excellent protection against corrosion of heated steel tubes and coupons in aqueous media, using a 100 ppm dosage, and applied in a pH range as low 5.0 and as high as 9.0.

Chromates and phosphates, both typical inorganic anodic inhibitors, have been used separately or in combination for corrosion prevention in cooling tower recirculation systems. When used alone the chromates required concentrations above 200 ppm as Na_2CrO_4. In combination with polyphosphates the total level of treatment is reduced to only 40-60 ppm. Chromates owe their protective action to their ability to form a thin, passivating film directly on the anodic portion of metal.

Besides chromates and phosphates (or their combinations) silicates, nitrites and ferrocyanides are also used. Salts of zinc, nickel, manganese and trivalent chromium are typical examples of cathodic inhibitors. These materials have the ability to form adherent, insoluble hydroxides at the cathodic area and thus cause cathodic polarization.

But the use of polyphosphates has drawbacks. They tend to hydrolyze and lose their sequestering ability. Besides this, they act as nutrients and accelerate the growth of slime or algae.

The U.S. Public Health Service recommends reduction of hexavalent chromium level to 0.05 ppm. Above this level it may have some toxic effect on humans, fish and marine life. New and more stringent pollution control laws are being adopted by the states as a result of the Water Quality Act of 1965, and therefore, most of the major treatment suppliers have non-chromic material on the market.

Summarizing, we can say that all of the commonly used corrosion inhibitor treatments based on chromates and phosphates at the present time can contribute to the pollution load, if the cooling water effluent is not diluate or treated properly before discharge. The economics of establishing waste treatment systems for treatment of chromates and phosphates may rule out their use. Therefore, it was decided to start on an extensive R&D program with the aim of producing a group of non-chromate corrosion inhibitors.

Nitrogen-containing, organic formulations

Over forty different nitrogen-containing organic-zinc formulations were screened, using a simplified version of cooling tower (see figure). Of this group only three materials showed promise which subsequently were formulated and tested in the experimental cooling tower. These materials will henceforth be identified as Inhibitor A, Inhibitor B and Inhibitor C. Inhibitors A and C consist of a blend of aromatic monocyclic nitrogen compounds with phosphonate and zinc. The difference between A and C lies in the percentage of the constituents. Inhibitor B consists of aromatic heterocyclic nitrogen compounds wiht phosphonate and zinc. For make-up Chicago tap water fortified with sodium chloride was used.

Experimental cooling tower

There are a wide variety of laboratory tests designed to evaluate the performance of corrosion inhibitors. The relative merits of some commonly known laboratory test methods used in the industry were studied by NACE Task Group T-5C-1. Their findings showed that only results obtained in dynamic tests correlated reasonably well with the results obtained from the pilot plant tests. Our corrosion tests were obtained in bench-scale test units designed by the staff of Wright Chemical. These units allow a close study of the variables such as temperature and pH, quality of water flow conditions, growth of scale, slime, and algae, inhibitors residual, amount of dissolved gases, etc. The system consists of a basin, a feed water tank, a centrifugal pump, glass jackets, a plexiglas tower and a mild steel heat exchanger. Chemical treatment and make-up water are fed continuously from chemical and feed water-tanks.

In this system heated tap water at 120 ± 3 F, was circulated at a velocity of one foot per second (approx). The temperature was obtained by the use of cartridge heaters. The desired number of cycles of concentration is obtained by adjusting the blowdown valve. The corrosion test specimens were C-1018 steel coupons 3 in. in length and 3/8 in. in diameter. These coupons were weighed before and after treatment. The loss in weight divided by duration of exposure was then extrapolated to give weight loss in mils/year. A C-1018 mild steel condenser tube, half inch O.D., used as heat exchanger, was also inserted. Corrosion of the tube was measured by visual and microscopic observation. The severity of corrosion was facilitated by adding sodium chloride to the circulating water.

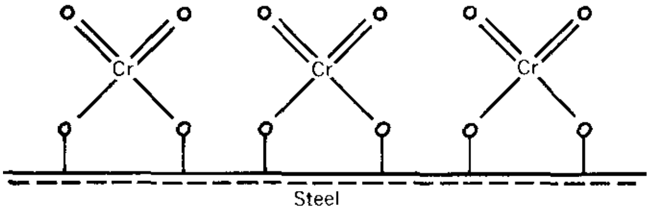
Performance under acid conditions

Laboratory tests performed in experimental cooling towers at 120 F and pH 5.0 to 6.5, exposed for 20 to 30 days, produced the following results on test coupons.

Inhibitor	Dosage ppm	Corrosion Rate mills per year	pH	NaCl ppm	Shock Treatments	Conc. Cycles
Control	0	375.3	5.6–6.3	250 to 290	–	4.0
Corrosion Inhibitor A	100	2.0	5.6–6.3	250 to 300	3.0	4.0
Corrosion Inhibitor	100	2.2	5.8–6.6	520 to 580	3.0	3.7–4.0

Mechanism of Inhibitive Action of Organic Corrosion Inhibitors

According to Uhlig(1) the protection of iron against corrosion by chromates is due to the formation of a surface compound. He believes that the bonding between e chromate and metal is chemical, but the metal lattice is intact, and no stoichiometric compound forms.



Surface compound formed by chromates.

A similar point of view was advocated by Rosenfeld and Akimov.(2) The alkali phosphates are considered to be less efficient inhibitors than chromates. The use of sodium hexamethaphosphate has been described in detail by Hatch and Rice.(3) Hatch(4) explains the protective action of phosphates towards steel is due to deposition of phosphate on the microcathode regions of the surface. This raises the cathodic polarization and simultaneously reduces the strength of the current involved in the corrosion processes. According to Hatch the formation of the protective film is a self-retarding process; the deposition of protective film reduces the current which causes its formation on the metal surface. It was found by Raistrick(5) that sodium tetrametaphosphate is not a corrosion inhibitor, and that trimetaphosphate is a weak inhibitor.

Polar organic compounds

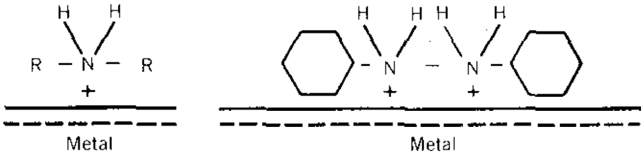
A literature study of local and foreign publications revealed that there exist a number of polar organic compounds which can be used as corrosion inhibitors. According to Mann and his associates(6, 7, 8) a group of nitrogen-containing materials especially aliphatic and aromatic amines give a good corrosion protection to metal in acid media. Mann, et al, believe that amine cations are absorbed on the cathodic regions of the metal surface, undergoing dissolution in such a way that a nitrogen atom is directly linked to the metal. A layer of amine cations, similar to the monomolecular layer, is formed on the metal surface, screening the metal surface and preventing the corrosion process from taking place.

In his book on the theory of corrosion protection, Tomashow(9) stated that a group of nitrogen containing organic materials gives a good corrosion inhibition in acid media. These materials act as principally anodic inhibitors. They shield the iron surface from the corrosive media. This group includes quaternary ammonium bases and their derivatives, B-naphthylamine, pyridine, quinoline, naphthaquinoline, naphthylquinoline, ortho-tolyl thiourea, aniline, ethylamine, diethylamine, acridine, acriflavin, etc. These materials are used for combating acid corrosion, as additives for pickling iron and steel in acids, and also for protection of vessels in storage and transportation of acids. It was anticipated that the addition of other organic materials and zinc ion should give protection to steel and iron and non-ferrous metals at a lower treatment level, to make this application feasible for cooling water treatment.

There was a disagreement on whether, in the case of acid attack, the inhibitors (e.g., amines and thioureas) act by retarding the anodic or the cathodic reaction, or whether they coat the surface generally and prevent replenishment of acid. Extensive work by Hoar and Holiday(10) has shown that there is interference with both cathodic and anodic reaction. The quinolines are primary anodic inhibitors, but at the high concentration they act as cathodic inhibitors. The thioureas inhibit both reactions – the cathodic reaction mainly at low concentration and the anodic reaction mainly at high concentration.

Adsorption theory

One of the first published works on organic nitrogen-containing corrosion inhibitors could be traced to the work of Sieverts and Lueg(11) who proposed the adsorption theory of protective activity. This theory was supported by Kreuzfeld(12) in his work on coal tar distillates as inhibitors for steel in sulphuric acid and Hoar(13) who studied the action of heterocyclic nitrogen bases, namely quinoline and acridine derivates. Hackerman and Markides(14) in their paper criticize the "overvoltage" theory and propose that inhibitor action results from the increased resistance to current flow caused by a barrier of physically adsorbed inhibitor and by reduction in metal reactivity by a chemi-sorbed inhibitor. A considerable amount of work was done on nitrogen-containing organic compounds by George and Hackerman,(15) Kohler and Brown(16) and Jones and Barett(17).



A protective layer of amine cations.

Kuznetsow and Jofa(18) stated that the ions of nitrogen-containing inhibitors are capable of being adsorbed predominantly on the most active regions of the dissolving metal, e.g., on the anodic areas. They propose that surface-active ions of the inhibitors change the adsorption potential of the metal, and that this leads to a change in the hydrogen overvoltage.

Overvoltage theory

In their investigation Kuznetsow and Jofa are supporting the "Overvoltage theory" called also the "Theory of Cathodic Action". This is actually not a new theory but was originated at a much earlier date by Worner(19), Tile and Kaiser(20), Mann, et al(6, 7, 8) and others. The essential of the overvoltage theory may be summarized as follows: Molecules, ions, or colloidal particles block the cathodic regions on the metal surface and raise the hydrogen overvoltage to such an extent that discharge of hydrogen ions can take place only very slowly. Retarding of the cathodic process leads, of course, to the same extent to retardation of the anodic process. This anodic retardation, however, is entirely due to the slower discharge of hydrogen ions and there exists no direct action of the inhibitors on the anodic reactions.

The theory of overvoltage (or cathodic activity) has been recently overthrown by the discovery that all organic inhibitors, without exception, act to a greater degree as polarizers of the anodic process than of the cathodic process. No direct relationship between the effectiveness of inhibitors and the rise in hydrogen overvoltage could be found. The film or chemisorption theory of inhibitive action was actively supported by Hackerman and Markides(14), Shilov, et al(21), Lepin(22), Dubinin(32), George and Hackerman(15), Cox, et al(24) and others.

Chemisorption theory

The proponents of the film theory believe that the effective protection of metals by inhibitors is due to the formation of a layer of products of reaction between the metal, the inhibitor, and the ions of the corrosive medium on the metal surface. Experiments have shown that all substances which are active corrosion inhibitors are capable of reacting with metal or its ions, forming insoluble or only slightly soluble compounds. Several investigators(14, 21, 22, 23, 15) classified this process as "chemisorption" – namely a process of adsorption on the surface by means of an heterogeneous reaction which gradually spreads over the whole surface. This means that the molecules of the surrounding medium react in this process with the molecules or atoms of the solid phase, producing a new substance in the form of an independent phase. (Example – oxygen reaction with copper turnings, formation of magnesium sulfate on MgO particles in a fluidized bed system, etc.) The process of chemisorption has often become much slower after a time, because such a compact layer of reaction product is formed on the surface that the molecules of the reacting media cannot penetrate.

Hackerman, Hurd and Annand(25) proved that inhibitor efficiencies within a series of cyclic imines and secondary amines show differences which are clearly related to differences in their molecular structure. Finley and Hackerman(26) investigated the inhibitor effectiveness in 1N acid solution using different polymethylimines. Their study included compounds with four to seven–CH_2–groups that showed an increase in inhibitor effectiveness with increasing ring size by about 20 percent per–CH_2–group. Stromberg(27) reported that in case of amino acids a slight difference in molecular structure in a long alkyl chain (like additional CH_2 group, etc.) does not affect the material to a great extent. Slight differences in the carbon chain between functional groups, however, result in more apparent differences.

Frenkhouser studied the inhibition with secondary acetylenic alcohols(28). His study indicated that 1-hexyn-3-ol and other secondary acetylenic alcohols can be efficiently used as acid corrosion inhibitors.

We would like to emphasize that nearly all of these inhibiting studies were done in acid solution and not in recirculating cooling systems where a much greater amount of oxygen and higher pH value prevail.

It is evident that the new non-chromate inhibitors A and B provide an excellent protection against corrosion of heated steel tubes and coupons, using 100 ppm dosage and acid conditions. The same materials were tested at the pH as low as 4.5-5.0 with excellent results.

Performance under alkaline conditions

Laboratory tests performed at 120 F and pH between 8.0 to 9.0 in experimental cooling towers produced the following results on coupons exposed for 20 to 30 da

Again, it is evident that Inhibitor C provides good protection against corrosion and scaling of heated steel tubes and coupons, using a 100 ppm dosage when applied under alkaline conditions.

It was also found that a high dosage of chlorine (as high as 20 ppm) did not adversely affect the performance of Inhibitor C. Therefore, it is safe to assume that the addition of chlorine does not increase corrosion. This is a very important point because of the susceptibility of most organic materials to chlorine.

Inhibitor	Dosage ppm	Corrosion Rate mills per year	pH	NaCl ppm	Shock Treatments	Conc. Cycles
Control	0	10.0	8.4–9.0	54 to 72	–	3.0
Corrosion Inhibitor C	100	1.0	8.4–9.3	50 to 75	4.0 4.0	3.5
Corrosion Inhibitor C	100	1.3	8.3–9.2	50 to 70	4.0	3.0

Because of the existing restrictions and limitations of conventional treatments a substantial demand for new non-chromate treatments is obvious. They should provide:

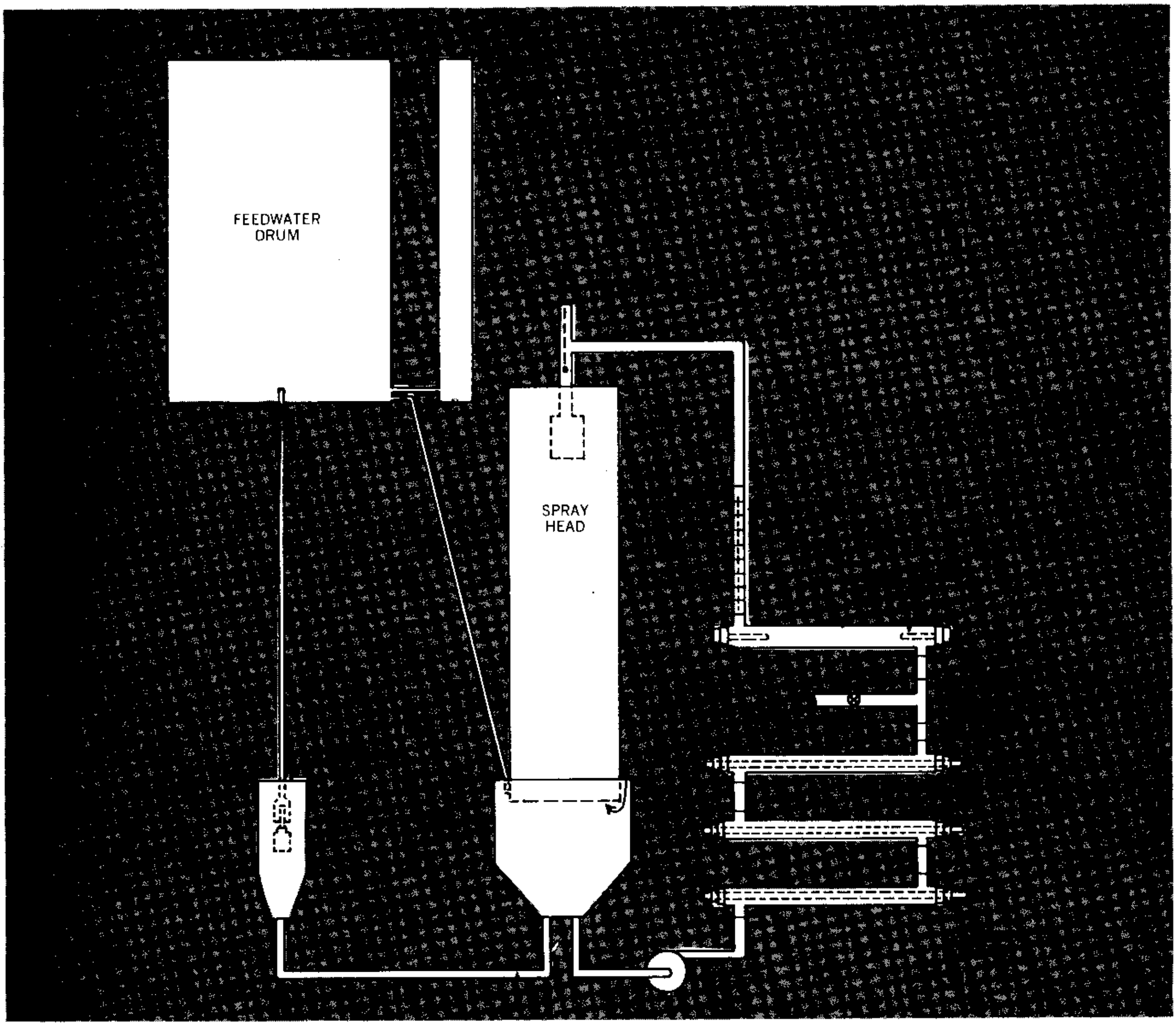
1. Effective corrosion inhibition.
2. Low toxicity of treatment combined with a low pollution load.
3. High stability.
4. Compatibility with chlorine and other biocides.
5. Preventive scale deposition in alkaline conditions.
6. Easy feed and control.

Results of this laboratory study and evaluation in the field show that the newly developed organic non-chromate inhibitors provide excellent protection against corrosion of steel surfaces.

These materials which are not subject to deposit formation from the inhibitor are low in toxicity and high in stability. They can be produced in ready to use liquid form, thus providing an ease of feed and control. They are also compatible with chlorine and other biocides.

Some case histories

☐ A chemical plant in Texas had operated their cooling towers successfully for years using a zinc-chromate-organic corrosion inhibitor. Corrosion rates of 0.5-0.8 mpy were normally encountered. The make up of these towers was



Laboratory cooling tower used to evaluate the non-chromate corrosion inhibitors consists of a basin, a feed-water tank, a centrifugal pump, glass jackets, a plexiglass tower and a mild steel heat exchanger.

clarified river water.

pH	7.4
Total Alkalinity	220 ppm
Calcium Hardness	190 ppm
Magnesium Hardness	66 ppm
Total Hardness	256 ppm
Sodium Chloride	18 ppm
Sodium Sulfate	25 ppm
Silica	2 ppm
Total Dissolved Solids	415 ppm

In early 1970 their engineering department decided to use one of their towers to "test" non-chromate inhibitors. Their purpose was to anticipate and prepare for possible restriction against chrome in their area. The tower selected had a circulation rate of 4,000 gpm and operated, normally, at a ΔT of 10-12 F.

The inhibitor chosen was a blend of silica, alkali and polyelectrolyte. Treatment was begun at a level of 150 ppm with no pH control (system pH averaged 8.1-8.2). Within a few days corrosion rates on a corrater began to give readings of 20-30 mpy. Finally, after 3 months, the "test" was discontinued. Average corrosion rate was 29 myp as determined by a corrater.

Next, Inhibitor A was tried. A treatment level of 100 ppm was maintained and pH control was enlisted to keep a range of 5.8-6.2 at all times. Treatment continued for six months. At no time did the corrater show rates higher than 1.8 mpy. At the end of the six month trial, the average corrosion rate from the corrater was 1.2 mpy. This was confirmed by coupons placed in the system at the initiation of the trial.

The plant has returned to the use of the zinc-chromate-organic inhibitor since the use cost is lower. They are ready, and, as a result of their testing, confident that they can go to the use of Inhibitor A, if and when it becomes necessary, due to pollution restrictions.

□ At a major defense contract facility on the west coast, the situation was one of urgency. They had just completed construction of a new plant in a suburban community when the community passed extremely rigid pollution control ordinances. To comply with these ordinances meant the elimination of the planned use of chromate inhibitors in the several medium size cooling towers located at the facility. The community supplied a make up water of the following quality:

pH	8.3
Total Alkalinity	124 ppm
Calcium Hardness	86 ppm
Magnesium Hardness	20 ppm
Total Hardness	106 ppm
Sodium Chloride	186 ppm
Sodium Sulfate	480 ppm
Silica	9 ppm
Total Dissolved Solids	819 ppm

Since a limit was also placed on the dissolved solids content of the plant effluent, it was decided to use Inhibitor C as the corrosion and scale inhibitor, with no pH control. The average tower had a circulation rate of 2,000 gpm with a 15 F temperature drop.

Treatment with Inhibitor C at 100 ppm has been in effect on a commercial basis for several months as of this writing. Corrosion rates have been as high as 2.3 mpy, but no higher. No scale is being encountered with the systems operating at 3 cycles of concentration.

□ Another example of awareness to possible future pollution restrictions involves a glass manufacturing plant in the south. This plant obtains all of its cooling water from a 500,000 gallon capacity spray pond. The water is circulated at a rate of approximately 3,000 gpm and is used in glass coolers to maintain the quality of the finished product. Corrosion and scale control are critical.

The spray pond had been treated for 8 years with a chromate inhibitor and pH control. In light of the increasing pollution awareness in the surrounding area, and because of occasional over-flowing of the pond, it was decided to embark on a program of non-chromate inhibition. With a make-up of the following quality:

pH	7.5
Total Alkalinity	35 ppm
Calcium Hardness	158 ppm
Total Hardness	180 ppm
Sodium Chloride	21 ppm
Sodium Sulfate	255 ppm
Silica	6 ppm
Total Dissolved Solids	331 ppm

It was decided to use Inhibitor C with muriatic acid for pH control. The muriatic acid was used rather than sulfuric acid to be certain that no excess sulfates were encountered which might lead to calcium sulfate scale (as previously stated, scale control was essential).

Treatment at 100 ppm at a pH level of 7.0-8.0 was begun. After a period of five months operation, coupons showed a corrosion rate of 1.1 mpy, and no scaling was encountered. The plant was advised that, should they wish, the use of acid could be discontinued. Since there was no automated pH control of acid addition, this suggestion was accepted readily.

To date, the system has operated with the same 100 ppm level of Inhibitor C and at a pH range of 8.1-8.8. Corrosion rates are being maintained at a level of around 1 mpy and no scaling problems are being encountered.

Additional formulations are presently under development and undergoing field testing to expand the capability to meet all pollution restrictions.

□

References

(1) H. H. Uhlig. Corrosion, 3, 1, 173 (1947)
(2) I. L. Rosenfeld and G. V. Akimov, "Investigations in the Corrosion of Metals" Izd. Akad. Nauk. S.S.S.R. vol. 1 p. 203 (1951)
(3) G. B. Hatch and O. Rice, Ind. Eng. Chem. 37, 710-715 (1945)
(4) B. B. Hatch, Ind. Eng. Chem. 44, 8, 1780-1786 (1952)
(5) B. Raistrick, Chem. Ind. 19, 408-414 (1952)
(6) C. A. Mann, Trans. Electrochem. Soc. 69, 115 (1936)
(7) C. A. Mann, B. E. Lauer and C. T. Hultin, Ind. Eng. Chem. 28, 2, 159-163 (1936)
(8) C. A. Mann, B. E. Lauer and C. T. Hultin, Ind. Eng. Chem. 28, 9, 1048-1051 (1936)
(9) N. D. Tomashow, "Theory of Corrosion and Protection of Metals" Book, p. 306. McMillan Company, New York, London (1966)
(10) T. P. Hoar and R. D. Holliday, J. Appl. Chem. 3, 502-513 (1953)
(11) Sieverts and Lueg, Zeitschrift anorg. Chem. 126, 193 (1923)
(12) W. Kreutzfeld, Korrosion und Metallschutz 4, 104 (1928)
(13) T. Hoar, "Proceedings of Pittsburgh Internat. Conference on Surface Reactions," Pittsburgh, Pa. Corrosion Publishing Co. p. 127-134 (1948)
(14) N. Hackerman and B. Markides, Ind. Eng. Chem. 46, 3, 523-527 (1954)
(15) R. A. George and N. Hackermann, Corrosion, 11, 6, 249t-254- (1955)
(16) H. L. Kahler and J. K. Brown, Combustion, 25, 7, pp. 55-58 (1954)
(17) W. E. Jones and J. P. Barrett, Corrosion, 11, 5, 217t-220t (1955)
(18) V. A. Kuznetsov and Z. A. Jofa, Zhurnal fiz. Khim. 21, 201 (1947)
(19) J. Worner, Trans. Amer. Electrochem. Soc. 55, 287 (1929)
(20) A. Tile and C. Kayser, J. Phys. Chem. 170, 516, 407 (1934)
(21) N. Shilov, E. Shatunovskaia and K. Chmutov, Zhurnal phys. Chem. 149, 211 (1930)
(22) L. K. Lepin, Usp. Khim. 9,5 (194)
(23) M. M. Dubinin, Usp. Khim. 24, 5 (1955)
(24) P. F. Cox, R. L. Every and O. L. Riggs, Corrosion 20, 9, p. 299t-302t (1964)
(25) N. Hackerman, R. M. Hurd and R. R. Annand, Corrosion 18, 1, 37t-42t (1962)
(26) H. F. Finley and N. Hackerman, I. Electrochem. Soc. 107, 4, 259-263 (1960)
(27) V. L. Stromberg, Materials Protection 4, 4, 60-64 (1965)
(28) J. G. Funkhouser, Corrosion 17, 6, 283t-287t (1961)

This article is based on a paper that was presented at the 32nd Annual Meeting of the International Water Conference of the Engineers' Society of Western Pennsylvania, Pittsburgh, Pa., Nov. 2-4, 1971.

KENNETH JURIS, Consolidated Edison of New York, Inc.

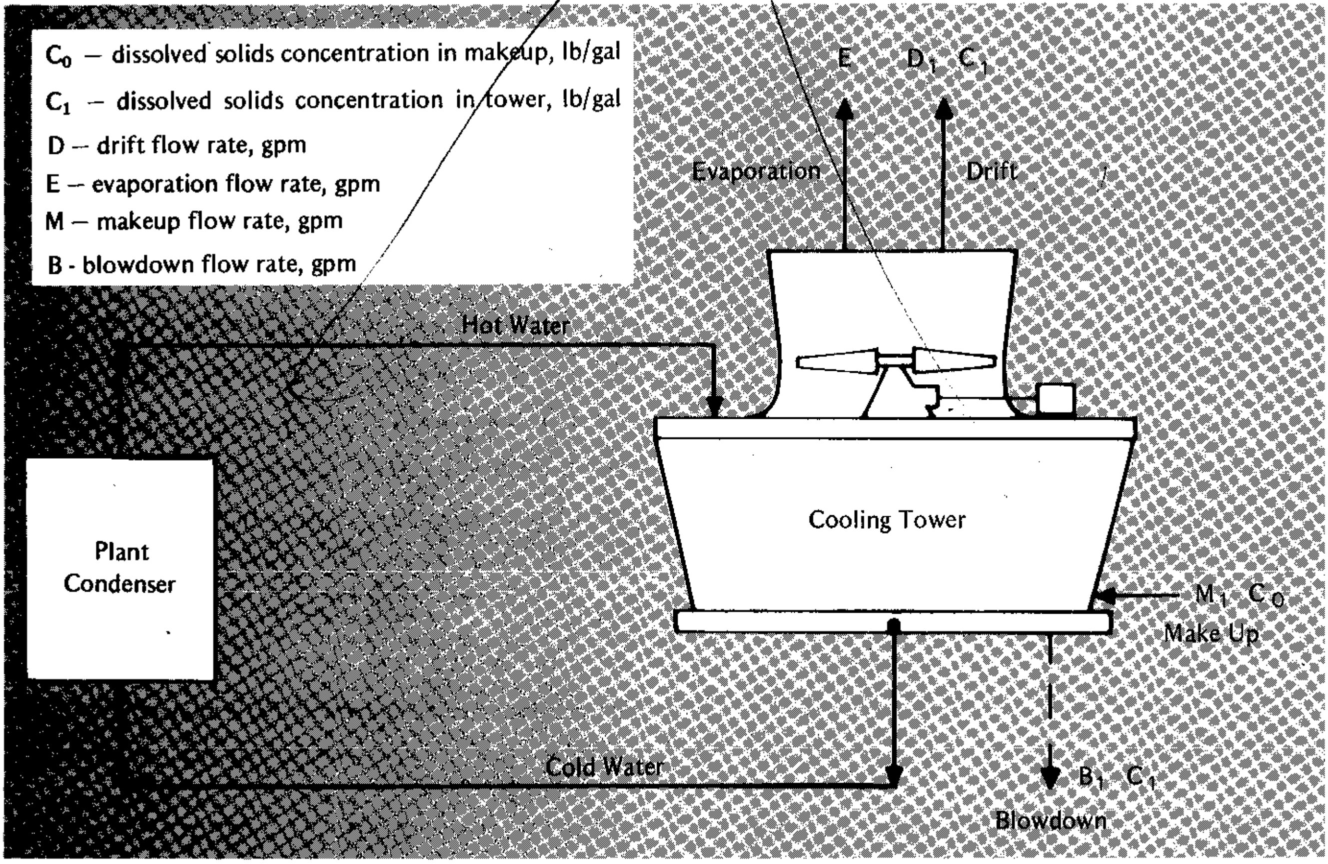
Simplified Method for Determining Tower Drift Rate

A simplified method is outlined for determining drift rates from cooling towers – both mechanical and natural-draft – and spray ponds. The only measurements required are the dissolved solids concentration of the makeup water and hot water recirculating back into the tower.

Five streams constitute the flow of water through a closed-cycle cooling system employing a mechanical-draft tower. They are the circulating, evaporation, drift, makeup and blowdown water flows. One of the five streams – the blowdown flow – is shut off in the method proposed below to determine the drift rate from the tower. When the blowdown flow is shut off, the concentration of dissolved solids in the recirculating water gradually increases; but contrary to what one might expect, this increase does not continue indefinitely. Soon a value C_1 is reached at which the rate of dissolved solids escaping in the drift equals the rate of dissolved solids entering the tower in the makeup flow. Moreover, the ratio of concentration of dissolved solids in the circulating and makeup water, C_1/C_0, is directly related to the drift rate. A high ratio indicates a low drift rate; conversely, a low ratio indicates a high drift rate.

Material balance

The above can be illustrated by a simple example. A mechanical-draft cooling tower with 600,000 gpm capacity is



Closed-cycle cooling system. The blowdown flow is shutoff to determine the drift-rate from the tower, which is why the blowdown is shown here as a dotted line. When the blowdown is shut off, the dissolved solids concentration of the recirculating water in the tower increases till it reaches a value C_1 at which point it levels off. At this point, the rate at which dissolved solids leave the tower is equal to the rate at which dissolved solids enter the tower.