$\underline{I}$ = electric flux vector component
$\bar{I}$ = mainstream electric flux vector components
k = thermal conductivity
K = electric conductivity
Nu_m = mean Nusselt number
Pr = Prandtl number
$\underline{q}$ = diffusive (also thermal) flux vector
q = diffusive (also thermal) flux
$\underline{Q}$ = mainstream diffusive (also thermal) flux vector component
Q = mainstream diffusive (also thermal) flux
r = radial distance
R = radius of reference sphere
Re = Reynolds number
S = radius of unit cell
t = temperature

Greek Letters, Operator Symbols

ϵ = porosity
θ = polar angle
ϕ = azimuthal angle
Λ_D = molecular (ionic) diffusivity factor = D^*/D^f
Λ_k = thermal conductivity factor = k^*/k^f
Λ_K = electric conductivity factor = K^*/K^f
∇ = del (gradient) operator
∇^2 = Laplacian operator

Subscripts and Superscripts

r = radial vector component
θ = polar vector component
f = designates fluid which saturates the porous medium
s = designates impermeable sphere
$*$ = designates macroscopically averaged quantities pertaining specifically to a porous medium

LITERATURE CITED

Bruggemann, D. A. G., "Berechnung verschiedener physicalischer Konstanten von Heterogenen Substanzen," *Ann. Physik*, **24**, 636 (1935).

De la Rue, R. E. and C. W. Tobias, "On the Conductivity of Dispersions," *J. Electrochem. Soc.*, **106**, 827 (1959).

Fricke, H., and S. Morse, "An Experimental Study of the Electrical Conductivity of Disperse Systems," *Phys. Rev.*, **25**, 361 (1925).

Hashin, Z., "Assessment of the Self Consistent Scheme Approximation: Conductivity of particulate Composites," *J. Comp. Mat.*, **2**, 284 (1968).

Klinkenberg, L. J., "Analogy between Diffusion and Electrical Conduction in Porous Rocks," *Bull. Geol. Soc. Am.*, **62**, 559 (1951).

Maxwell, Clerk, Electricity and Magnetism, 3rd ed., 435, Clarendon Press, Oxford (1892).

Nader, W. K., "Potential Distribution Near a Perforated Well," M.Sc. thesis, Univ. Texas, Austin (1960).

Prager, S., "Diffusion and Viscous Flow in Concentrated Suspensions," *Physica*, **29**, 129 (1963).

Rayleigh, Lord, "On the Influence of Obstacles arranged in Rectangular Order upon the Properties of a Medium," *Phil. Mag.*, **34**, 481 (1892).

Schlichting, H., Boundary Layer Theory, 6th ed., McGraw-Hill, New York (1968).

Schofield, R. K., and C. Dakshinamurti, "Ionic Diffusion and Electric Conductivity in Sands and Clays," *Faraday Soc. Disc.*, **3**, 56 (1948).

Wyllie, M. R. J., and A. R. Gregory, "Formation Factors of Unconsolidated Porous Media," *Trans. AIME*, **198**, 103 (1953).

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Dropwise and Filmwise Condensation of Water Vapor on Gold

A pure gold tube was found to give filmwise condensation in the absense of organic contamination in a flow situation simulating that found in seawater conversion plants. A sensitive test for the presence of organic contamination has been developed. The gold tube, promoted by paraffinic thio-silane or mercaptan, gave 100% excellent dropwise condensation. Overall heat transfer coefficients are reported for filmwise and dropwise condensation. The steamside heat transfer coefficient with dropwise condensation was estimated to be over 0.2 MW/m^2-°C (35,000 B.t.u./hr-ft^2-°F) at the 95% confidence level.

Gold plated tubes* gave 95% filmwise condensation after one week of operation in a clean, once-through system.

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SCOPE

Water vapor can condense as a continuous film or in discrete drops. The latter can result in greatly enhanced heat transfer. Noble metals such as gold have been reported as giving permanent dropwise condensation and gold plated tubes have been proposed for use in seawater conversion plants. Permanent dropwise condensation would also be very desirable for fundamental studies of the dropwise phenomena because variables such as promoter quality, life, thickness, and time dependence could

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* Supplied by P. Tomalin and S. Mulford of the Office of Saline Water, USDI.

be eliminated in interpreting results from different investigators. Recent workers have shown that gold is inherently wetting. This investigation was conducted to determine the mode of condensation that a solid gold or gold-plated tube would give under conditions simulating those found in seawater conversion plants.

CONCLUSIONS AND SIGNIFICANCE

Pure gold was found to give film-type condensation in the absence of organic contamination. Dropwise condensation was achieved by adding a small amount of promoter. Lauryl mercaptan, n-octadecyl mercaptan, and tetrakis octadecylthiosilane were excellent promoters for dropwise condensation on gold although their life was shorter than on copper.

Although bright gold-plated tubes that had been previously installed in a seawater conversion plant remained more or less nonwetting at zero flux during testing in our apparatus, the low water contact angle resulted in filmwise condensation at reasonable heat fluxes. This nonwetting behavior was attributed to the presence of traces of organic brighteners from the plating bath remaining trapped interstitially in the gold lattice.

Overall heat transfer coefficients were measured with the pure gold tube for cooling water velocities of from 2 to 8 m/sec for both dropwise and filmwise condensation. With dropwise condensation on pure gold the steamside heat transfer coefficient was high—at least 0.2 MW/m^2-°C (35,000 B.t.u./hr-ft^2-°F).

We conclude that gold will give film-type condensation in seawater conversion plants unless some drop promoter is present or added.

Because of our work with dropwise condensation we became interested in the wettability of solid surfaces. Fox and Zisman (1950) and Fox et al. (1955) classified surfaces as either high or low energy according to their wettability and concluded that all pure liquids spread spontaneously on high energy surfaces except for a special class of organic liquids. Pure water should spread, then, on any clean high energy surface such as pure metals.

Erb (1965) and White (1964) reported that water vapor condensed in a dropwise fashion on gold and stirred interest in the inherent wettability of gold. At the same time Fowkes (1964) postulated a theoretical basis for this phenomenon. Erb continuously condensed water vapor on several metals. After several thousand hours, noble metals such as gold continued to maintain dropwise condensation while base materials, such as titanium and glass, condensed in a filmwise manner. White condensed water vapor on gold foil from air saturated with water vapor at one atmosphere in an all-pyrex and metal system. He concluded that water should not spread in the absence of a layer of gold oxide. Using a sessile drip technique Bewig and Zisman (1965) stated that water spontaneously spreads on a clean surface of pure gold. To remove organic contamination they heated their sample to near its melting point in flowing streams of high purity gases. These gases contained trace impurities that were gradually adsorbed by the gold and would render the surface nonwetting after extended exposure. Both White and Drobek (1966) and Erb (1968) stated that residual inorganic contamination could result in a lower contact angle of water on gold. Recently Bernett and Zisman (1970) reported that water spreads on gold. Great care was taken to avoid trace organic contamination as well as to eliminate any residual inorganics on the polished gold surface. Concurrently Schrader (1970) used a vapor-phase transfer technique and showed that water wet pure gold that had been evaporated in situ in an ultrahigh vacuum system.

We were interested in gold surfaces for dropwise condensation in seawater conversion plants because Erb and Thelen (1965) had recommended thin gold-plating for achieving permanent dropwise condensation.

EXPERIMENTAL APPARATUS

General

The apparatus used in this study has been described previously (Bromley et al., 1968) and consisted basically of a vertical condenser with an active tube length of 1.42 m housed in 76.2-mm diam. glass pipe. Water vapor at one atm. was generated by boiling fresh seawater by indirect contact with steam generated by an external boiler. The feed seawater had been filtered, *p*H adjusted, and degassed. Distilled water was circulated through the condensing section in a closed loop. Excess brine and the condensate were sent to drain. Promoters were injected into the seawater boiler by means of a hypodermic syringe.

Inlet and outlet cooling water temperatures were measured in insulated mixing chambers with Hewlett-Packard quartz thermometers, absolute accuracy ± .01°C; in addition, thermocouples were used. The cooling water flow was read from a calibrated rotometer. A short-range mercury thermometer was read to 0.01°C for the steam temperature.

Gold Tube

The tube used in this work was 15.9-mm (5/8 in.) O.D., 0.89-mm (0.035 in.) wall-thickness solid gold. This tube was extruded from 99.95% pure gold; the only lubricant applied during the extrusion was Ivory soap.

REMOVING ORGANICS

Previously this apparatus had been used to test promoters on copper. Since promoter molecules would probably remain in the system, a method of removing them and a sensitive test for their presence has been developed.

Clean bright pink copper was found to be sensitive to low levels of organics; however, significant amounts of the best promoters could be present and the copper would remain filmwise. This is believed to be caused by the fact that during filmwise condensation the promoter molecules in the steam strike and remain at the water-steam interface and are swept away (Bromley et al., 1968; Blackman and Dewar, 1957). If this water film is broken for a few minutes, then any promoter molecules coming over have a chance to attach to the copper surface. An effective way to do this is to inject a few cc's of a quick but short-lived promoter. Octanoic acid rapidly promotes copper to good dropwise condensation but has a life of less than 5 minutes for a single injection of 1 cc. If no organics were present the copper would revert to filmwise condensation; dropwise condensation would be maintained, however, if promoter molecules were present. With very low levels of organics present all but a few spots would revert to filmwise after injecting the octanoic acid. These spots would then slowly grow until in a matter of hours the whole tube would be dropwise.

To remove the last traces of organics it was necessary to run the apparatus for a week or more. The apparatus was repeatedly flooded with hot, foamy, acidified seawater during this period by injecting a few cubic centimeters of a good foamer directly into the boiler.

When repeated tests of pink copper, promoted by injecting octanoic acid, reverted to 100% filmwise the system was deemed free of organic promoters and tests with the gold tube were begun.

RESULTS

Filmwise

The gold tube was installed as received. Care was taken not to contaminate the tube as it was being installed. When steam was admitted the gold was weakly nonwetting. Several small drops would coalesce into one glob that had no distinct boundaries and slide down the tube. The cooling water was started and the tube changed to filmwise condensation. At the end of about 10 minutes the tube was 100% filmwise and remained so for several hours at which time the apparatus was shut down for the day.

The gold tube continued to give filmwise condensation for a period of two weeks, being shut down at night and started again in the morning. Occasionally a small spot or two near the top of the tube would go dropwise. These spots would persist for a few hours at most.

The water film showed no tendency to fracture when either the steam or the cooling water were turned off. After standing overnight, however, some parts of the tube would be weakly dropwise until the cooling water was turned on.

Dropwise

After establishing the fact that gold does give filmwise condensation we decided to test various promoters for dropwise condensation on the gold tube.

Octanoic acid was the first promoter that was tested. Injecting about 1 cc directly into the boiler caused the whole tube to go to good dropwise that faded rapidly to filmwise in less than 5 minutes. This also served to demonstrate that the system was free of organic contamination.

Oleic and stearic acid were also tested and found to be very poor promoters on gold. Large quantities (10 cc) of oleic acid had to be injected to achieve dropwise condensation on the entire tube. This faded quickly.

Compounds that were known to be excellent promoters on copper were tried. Tetrakis octadecyl thio-silane, $(C_{18}H_{37}S)_4Si$, has been reported by Bromley et al. (1968) as the best promoter on copper. A 1% solution in 2-ethylhexanoic acid was prepared and ½ cc was injected into the boiler. This gave excellent dropwise condensation on the gold that lasted about 12 hours before returning to 100% filmwise at a flux of 0.25-0.32 MW/m^2 (80,000 to 100,000 B.t.u./hr-ft^2). Mercaptans were reported by Blackman and Dewar (1957) and Bromley et al. (1968) as being good promoters for copper. One cc of lauryl mercaptan $C_{12}H_{25}SH$, a liquid at room temperature, gave excellent dropwise condensation that lasted 8 hours before any spots became wetting at a flux of 0.25 to 0.32 MW/m^2. By the end of another day 95% of the tube was filmwise. A 50-50 mixture, a liquid at room temperature, of n-octadecyl mercaptan, a solid at room temperature, and lauryl mercaptan also gave excellent dropwise condensation with a somewhat longer life.

These compounds were judged to be about equal in promoter quality. The mercaptans were easier to apply and cheaper than the thio-silane.

Promoter Removal

After measuring dropwise coefficients the equipment was operated at low flux (0.047 MW/m^2) without adding additional promoter. After two weeks of operation during the day and shutting down at night the gold tube was 50% filmwise. By the end of the third week 90% of the tube was filmwise. The portion remaining dropwise was the bottom 6 in. of the tube. This area would flood out if the flux were increased to about 0.08 MW/m^2.

That the bottom of the tube is the last area to go filmwise is consistent with these observations:

1. Promoter molecules tend to migrate down the tube.
2. The colder a section, the longer a promoter will stay on the tube.

Gold reverting to film-type condensation in a once-through system, after being promoted to excellent drop-type condensation, confirms the inherent wettability of gold when free of organic contamination.

Gold Plated Tubes

Two gold plated tubes 15.9 mm O.D., 1.07 m long were obtained from the Office of Saline Water. These tubes had been installed previously as part of the 16th stage of the Senator Clair Engle Test-Bed Plant's first effect. One tube was described by Mulford (1971) as giving good dropwise condensation and the other poor dropwise at the time they were removed. They had been installed in a horizontal position. As received, these tubes were covered with a thin layer of brown powder that was probably iron oxide. This powder was quite loose and most of it adhered to the plastic the tubes were wrapped in.

The tubes were tested individually in our apparatus. One tube had about 20% dropwise, the other 10% when first tested at a flux of 0.03 MW/m^2. Over a period of a week this decreased to 5% for both tubes. This portion would go filmwise if the flux were increased to 0.06 MW/m^2.

The water film would fracture in about 60 seconds if the cooling water were stopped. The pure gold tube had not shown any tendency for the water film to fracture under the same conditions. The plated gold, then, was nonwetting but with such a low water contact angle that the tube would flood easily.

This difference in the wettability of pure gold and plated gold indicates organic contamination of the plated gold. The most probable source of this contamination is the plating bath. Bright gold plating baths, such as Technic Orosene 999 recommended by Erb, et al. (1969) contain proprietary organic brighteners whose function is to orientate the gold atoms in the lattice sites and thereby achieve a bright plate. The brightener remains trapped interstitially in the gold lattice. This renders the plated gold nonwetting. After many hours of condensing the brightener is leached out of the surface layer and the dropwise condensation fades to filmwise condensation provided no other organics reach the surface.

HEAT TRANSFER MEASUREMENTS

Overall Coefficients

Overall heat transfer coefficients were measured for both filmwise and dropwise condensation as a function of cool-

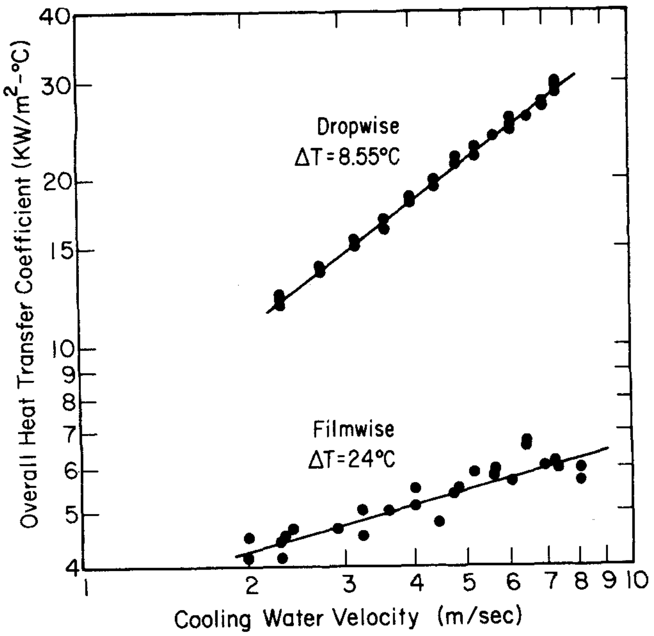

Fig. 1. Overall heat transfer coefficients for dropwise and filmwise condensation of steam on a pure gold tube.

ing water velocity. These results are summarized in Figure 1. The overall dropwise coefficients are considered to have an error of ±2%; the filmwise coefficients are ±10%. The increased accuracy of the dropwise data was due to using quartz thermometers instead of thermocouples to measure the cooling water temperature.

Lauryl mercaptan was the promoter used to obtain dropwise condensation. After about 4 hours the part of the tube facing the vapor inlet would start to wet out due to erosion by the wet steam. Small amounts of promoter (¼ cc) were injected into the boiler to restore this part to 100% excellent dropwise condensation.

Steamside Coefficient

The steamside (or outside) coefficients with dropwise condensation for copper in a vertical position have been reported, and the influence of heat flux, promoter used, and time upon the coefficients has been investigated by other workers. Le Fevre and Rose (1965) determined the effect of flux and promoter; Tanner et al. (1965a) also reported the effect of flux on the steamside coefficient. These two effects, heat flux and promoter, are small over the range of heat flux (0.08-0.25 MW/m^2) in this work and are within the experimental error of our results.

The time variation of the steamside coefficient can be significant. After an application of promoter, Tanner et al. (1965b) found the steamside coefficient increases with time, then remains constant, and finally falls off. With stearic acid the coefficient reached a maximum in about 10 minutes; montanic acid and dioctadecyl disulfide required 1 hour to reach a maximum. The time dependence of dioctadecyl disulfide was also investigated by Citakoglu and Rose (1968). They reported the steamside coefficient increased for about three hours and remained constant for five hours and then decreased slowly. This initial increase of the steamside coefficient was attributed to the thermal resistance of an excess layer of promoter and its subsequent removal by the condensate. The longer time required for the steamside coefficient to reach a maximum could be due to either a thicker initial layer or vapor phase return of promoter.

The time dependence of the steamside coefficient with lauryl mercaptan, the promoter used in the heat transfer measurements, was investigated. A constant value for the steamside coefficient was reached in 30 to 45 minutes.

Considering these effects the steamside coefficient was taken to be a constant for the purpose of estimating it from our experimental results for the overall coefficient.

Over a limited range of Reynolds numbers, the Nusselt number involving the inside coefficient can be expressed as a simple power function of the Reynolds number at a constant Prandtl number as

$$N_{Nu} = CN_{Re}^{\eta}$$

Assuming a constant value for the outside coefficient a water side or inside coefficient can be calculated for each experimental overall coefficient since the thermal conductivity of gold is well known. If these inside coefficients are fit to a simple power function expression the exponent η can be determined by the method of least squares. Each assumed value of the outside coefficient yields a different value for η.

The variation of Nusselt number with Reynolds number and Prandtl number has been correlated by Deissler (1955). Considering both the error in Deissler's correlation and in our experimental results, confidence limits were placed on the outside coefficient by comparing Deissler's values for η ($\eta = .82 \pm 5\%$) with those calculated from the experimental results. At the 95% confidence level the lower limit on the outside coefficient was

$$ho = 0.2 \text{ MW/m}^2\text{-°C } (35{,}000 \text{ B.t.u./hr-ft}^2\text{-°F})$$

This coefficient also includes any resistance due to fouling although there should be none.

This lower limit is smaller than reported by Le Fevre and Rose (1965) and Tanner et al. (1965a) for copper.

ACKNOWLEDGMENT

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NOTATION

C = constant
ho = steamside heat transfer coefficient
N_{Nu} = Nusselt number
N_{Re} = Reynolds number
η = exponent on Reynolds number

Conversion Factors

$MW/m^2 \simeq 0.317 \times 10^6$ B.t.u./hr-ft²
$MW/m^2\ °C \simeq 0.176 \times 10^6$ B.t.u./hr-ft²-°F

LITERATURE CITED

Bernett, M. K., and W. A. Zisman, "Confirmation of Spontaneous Spreading by Water on Pure Gold," *J. Phys. Chem.*, **74**, 2309 (1970).

Bewig, K. W., and W. A. Zisman, "The Wetting of Gold and Platinum by Water," *ibid.*, **69**, 4238 (1965).

Blackman, L. C. F., and M. J. S. Dewar, "Promoters for the Dropwise Condensation of Steam. Part IV. Discussion of Dropwise Condensation and Testing of Compounds," *J. Chem. Soc. (London)*, 171 (1957).

Bromley, L. A., J. W. Porter, and S. M. Read, "Promotion of Drop-By-Drop Condensation of Steam from Seawater on a Vertical Copper Tube," AIChE J., 14, 245 (1968).

Citakoglu, E., and J. W. Rose, "Dropwise Condensation—Some Factors Influencing the Validity of Heat-Transfer Measure-

ments," *Intern. J. Heat Mass Transfer*, **11**, 523 (1968).
Deissler, R. G., "Analysis of Turbulent Heat Transfer, Mass Transfer, and Friction in Smooth Tubes at High Prandtl and Schmidt Numbers," N.A.C.A. Report 1210 (1955).
Erb, R. A., "Wettability of Metals under Continuous Condensing Conditions," *J. Phys. Chem.*, **69**, 1306 (1965).
———., "The Wettability of Gold," *ibid.*, **72**, 2412 (1968).
———., T. I. Haigh, and T. M. Downing, "Permanent Systems for Dropwise Condensation for Distillation Plants," paper presented at Symp. on Enhanced Tubes for Desalination Plants (1969).
Erb, R. A. and E. Thelen, "Promoting Permanent Dropwise Condensation," *Ind. Eng. Chem.*, **57**, 49 (1965).
Fowkes, F. W., "Attractive Forces at Interfaces," *ibid.*, **56**, 40 (1964).
Fox, H. W., E. F. Hare, and W. A. Zisman, "Wetting Properties of Organic Liquids on High Energy Surfaces," *J. Phys. Chem.*, **59**, 1097 (1955).
Fox, H. W., and W. A. Zisman, "The Spreading of Liquids on Low Energy Surfaces. I. Polytetrafluoroethylene," *J. Colloid. Sci.*, **5**, 514 (1950).
Le Fevre, E. J., and J. W. Rose, "An Experimental Study of Heat Transfer by Dropwise Condensation," *Intern. J. Heat Mass Transfer*, **8**, 1117 (1965).
Mulford, S., Office of Saline Water, San Diego Test Facility, private communication (1971).
Schrader, M. E., "Ultrahigh Vacuum Techniques in the Measurement of Contact Angles. II. Water on Gold," *J. Phys. Chem.*, **74**, 2312 (1970).
Tanner, D. W., C. J. Potter, D. Pope, and D. West, "Heat Transfer in Dropwise Condensation—Part 1. The Effects of Heat Flux, Steam Velocity and Non-Condensable Gas Concentration," *Intern. J. Heat Mass Transfer*, **8**, 419 (1965a).
———., "Heat Transfer in Dropwise Condensation—Part II Surface Chemistry." *ibid.*, **8**, 427 (1965b).
White, M. L., "The Wetting of Gold Surfaces by Water," *J. Phys. Chem.* **68**, 3083 (1964).
———., and J. Drobek, "The Effect of Residual Abrasives on the Wettability of Polished Gold Surfaces," *ibid.*, **70**, 3432 (1966).

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Suboptimal Feedback Control of Distributed Systems:

Part I. Theoretical Developments

A new method for suboptimal feedback control of certain classes of distributed systems based on successive instantaneous minimization of the performance functional kernel is presented. This method is applicable to both linear and nonlinear systems.

The Lyapunov functional approach is extended to distributed systems, yielding two new suboptimal feedback control techniques. Also, an application of multilevel bang-bang control to the first-order hyperbolic system is presented and generalized.

Advantages and disadvantages of the suboptimal control techniques vis á vis open loop optimal control methods are listed, as well as comparative features of the suboptimal control methods.

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SCOPE

Many processes encountered in engineering practice possess significantly nonuniform spatial distributions in the values of their state variables. In modeling the unsteady state behavior of such systems, the use of partial differential equations is very desirable. Although ensuring an accurate representation of system behavior, the use of a distributed model makes the synthesis of an optimal control policy for the system extremely laborious. Furthermore, except in one special case, the optimal control must be applied to the system in a feedforward manner. Feedforward control is plagued by many shortcomings, rendering it unsatisfactory for many practical applications.

The objective of this work is to develop feedback control algorithms for distributed systems which provide near-optimal control, yet which are conceptually simple and flexible enough to have potential for practical use.

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