Dropwise Condensation on Gold

IMPROVING HEAT TRANSFER IN STEAM CONDENSERS

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A new and potentially large-scale use of gold is in coatings to cause steam to condense in the form of drops instead of in the usual form of continuous films. The consequent increase in heat transfer that could be achieved could lead to reductions in both the size and the cost of equipment for desalination and for power generation.

It has been known since the pioneering work of Schmidt, Schurig and Sellschopp (1) some 40 years ago that a much higher overall heat-transfer coefficient is obtained when water can be made to condense in drops rather than in the usual continuous film. A thick film of water, which has low thermal conductivity, acts as an insulating blanket in filmwise condensation; the field of mostly microscopic drops in dropwise condensation avoids this. In spite of the long-term knowledge about the increased condensing efficiency with dropwise condensation, the filmwise mode continues to be used in all commercial practice.

Why is this? One reason has been the lack of a suitable, permanently dropwise-promoting surface for condenser tubes. The usual approach has been the addition of organic promoters, materials which will chemisorb on the substrate. Examples of these for copper-alloy substrates are organic acids (2) and large organic molecules with multiple sulphur linkages (3). These have the disadvantage of having temporary effectiveness, with repeated additions being necessary. Another general approach has been to apply thin coatings of polymers such as silicones or polytetrafluoroethylene to the condenser surface. Since organic materials have low thermal conductivity, a major problem lies in producing polymer coatings thin enough not to retard heat transfer, yet with complete surface coverage, adequate adhesion, and mechanical integrity.

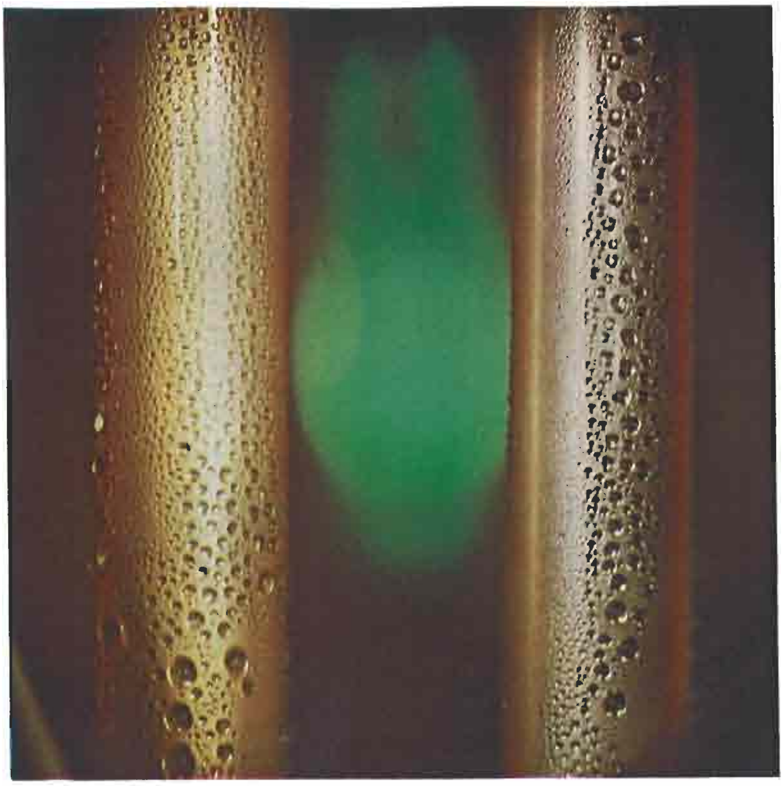
Early Studies on Inorganic Coatings

In 1962, The Franklin Institute Research Laboratories, under the sponsorship of the Office of Saline Water, United States Department of the Interior, undertook a study from a different direction. The programme was directed toward producing permanent dropwise condensation by application of *inorganic* coatings. The materials initially studied were metallic sulphides and selenides (4). Particularly of interest were Cu_2S and Ag_2S, which had been reported to be hydrophobic and to have low solubility in water (about 10^{-12} moles/litre at 100°C).

In the early course of the eight-year programme at the Franklin Institute, a strange discovery was made. We had been reacting various copper alloys and silver with hydrogen sulphide in moist air to form sulphided surface layers in controlled thicknesses. These sulphided specimens and corresponding unsulphided controls were then tested under continuous condensing conditions in air-free steam. The strange phenomenon observed was that the unsulphided silver surface (quite unlike the unsulphided copper alloys) promoted dropwise condensation. Indeed, over long terms of continuous condensation, the bare silver matched the dropwise performance of the best sulphided surfaces. The dropwise behaviour indicated that water has a rather high contact angle on a clean silver surface. (The contact angle is the angle, measured within the drop, between the substrate plane and a tangent to the drop at the intersection of the drop surface with the plane.) This was strange to us because we believed at the time that clean, high-energy surfaces (including those of metals and metal oxides) were inherently wettable by water, with the contact angle being zero. Thinking the dropwise behaviour might be caused by organic contamination, we took many pains to clean the apparatus and the distilled water used for reflux condensation, yet the silver remained dropwise.

The Superiority of Gold

The next step was a prediction. If silver was inherently dropwise, as it by now appeared to be, then from the Periodic Table—copper, silver, gold—if copper is filmwise, and silver is dropwise, then gold should be even better than silver in promoting dropwise condensation. Experiments on both solid gold and gold-plated samples showed this to be true. A factor in the superiority of gold is that the silver surfaces tended to roughen with extended condensa-



Dropwise condensation in steam at 114°C on gold-plated cupro-nickel tubes (left) and on tubes coated with a vapour-deposited polymer (right). The electro-deposited gold surfaces have longer lives and higher heat transfer coefficients than polymer coatings. A great deal of development work remains to be done to bring this unique property of gold to full scale application, but there is good reason to believe that it will be rewarded with a significant advance in the technology of heat transfer

tion of steam from sea water, which adversely affected wettability; this did not occur with gold. Figure 1 shows dropwise condensation on a gold surface and on a polymer surface in steam generated from sea water.

Although we later showed that platinum metals—notably palladium and rhodium—also promoted dropwise condensation, the dropwise quality was less consistently good than was the case with gold. Patents, assigned to the United States of America as represented by the Secretary of the Interior, have been issued on the promotion of dropwise condensation by silver (5), gold (6), and the platinum metals (7).

Cause of the Non-wetting Behaviour

In the course of our experimental programme the key to dropwise behaviour seemed always to be associated with the presence of oxide-free metal surfaces. Many metals other than the noble metals were studied as condensing surfaces but none was successful for long-term dropwise behaviour. If the surface is oxide-free initially, as gold basically is, or if the surface oxides or hydrated oxides wash off under continuous condensation and don't re-form, as is possibly the case with other noble metals in air-free steam, then there exists a surface to which water can bond only weakly. That is, only dispersion-type interactions are possible rather than the stronger hydrogen-bond-type interactions.

Considerable controversy has occurred and still exists in the scientific community about the wettability of gold. One school of thought suggests that clean gold surfaces are inherently non-wettable by water. White (8, 9) and Erb (10, 11) present evidence for this in a variety of carefully controlled experiments. A value of about 62° for the contact angle of water on gold is supported. A value of this magnitude is consistent with theoretical considerations of Fowkes (12, 13) and Thelen (14) on dispersion-force interactions in the interfacial relationships of water with oxide-free metal surfaces.

The other school, in papers by Bewig and Zisman (15), Bernett and Zisman (16), and Schrader (17), supports experimentally the view that the contact angle of water on clean gold is zero. The contention of these investigators is that the high angles are simply due to organic contamination—this in spite of radiochemical evidence (11) that organic contaminants are adsorbed more weakly on gold than on metal oxides. Non-equilibrium measurement conditions (the atmosphere about the drop not being saturated with water vapour) and contamination with oxides of base metals may be the causes of the measured zero angles. To resolve decisively the controversy there are other experimental approaches which exhibit promise, if funds could be obtained for carrying them out.

Studies (18) were carried out on the microcondensation phenomena involved in dropwise condensation. After large drops under gravity sweep the surface, heterogeneous nucleation occurs to form a new field of drops at distinct and repeatable sites;

these drops grow with successive mergings before forming drops visible to the naked eye. Sites, which might be concavities such as etch pits, vary in their ability to cause nucleation of water vapour; sites can be catalogued according to the required supersaturation ratio for condensation to occur.

Practical Coating Systems

Dropwise condensation has been shown to continue on a solid gold specimen and a copper-alloy specimen plated with a heavy layer of gold (50 micrometre) for 5.7 years before the tests were terminated, in a refluxing apparatus. However, at least for large-scale desalination applications, cost is the overriding factor. That is, the reduction in capital cost by reducing the tubing and shell required must not be exceeded by the cost for materials and application of the coating system on the reduced surface area of tubing (19). Coatings of gold, applied in one and two layers to a total thickness of 0.5 micrometre, did enter the economically attractive range. However, these coatings, using nickel undercoatings, would form microblisters, followed sometimes by localised flaking, and a deterioration of the dropwise quality (base-metal contamination), such that none performed satisfactorily for more than two years.

A much more satisfactory system consists of a very thin layer of gold over a much thicker layer of silver. The silver barrier layer restricts migration of base metals to the surface; the gold provides the dropwise surface and protects the silver against chemical roughening. From two-year 'wear-away' studies with gold top-coats only 0.025 micrometre thick, it appears that 20-year lifetimes might be obtained with the recommended 0.25 micrometre thickness. Recommendations for coating system and procedure are as follows:

(1) Substrate preparation: polish or buff, if needed, to ensure a specular finish on deposited coatings; clean by technique (solvent, detergent and/or chemical cleaner) recommended for the particular alloy and nickel coating used;

(2) Electrodeposition: 12.7 micrometre of bright nickel, using manufacturer's recommended current density, temperature, agitation, and anode material; 6.4 micrometre of bright silver, using manufacturer's recommendations; 0.25 micrometre of bright high-purity gold, using manufacturer's recommendations.

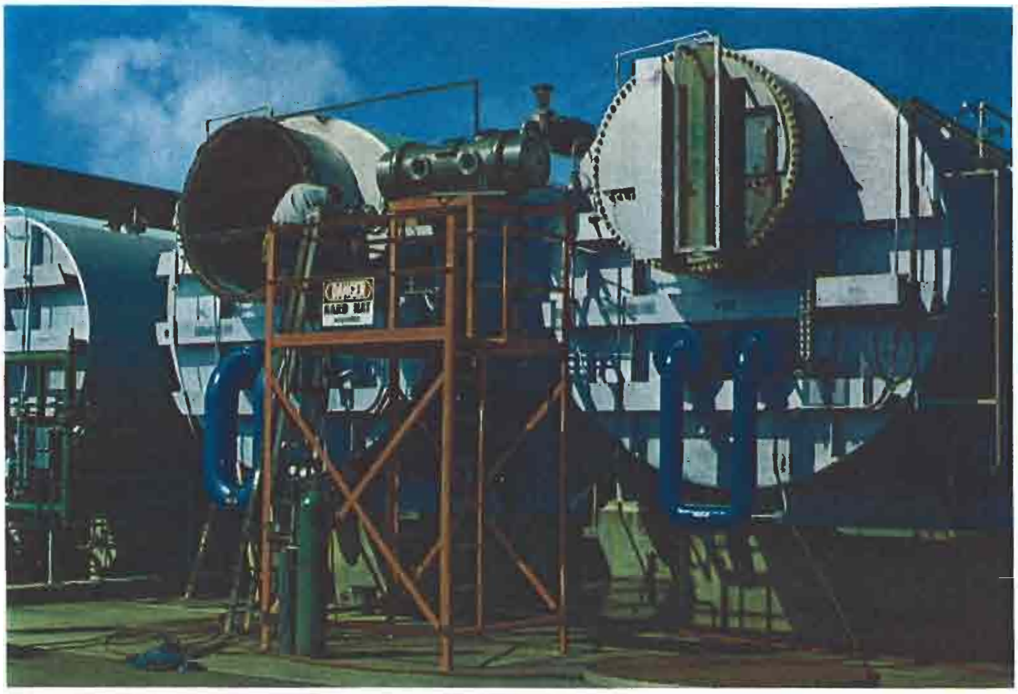
(3) Post-coating: Deposition of water-soluble polymeric protective coating (e.g., hydroxypropyl methyl cellulose). This last step is to prevent scratching of the tubes during shipment and installation. A scratch through to the base metal is not a serious problem, as was seen when such a scratch was deliberately made, followed by 2192 hours of condensation; no localised corrosion or other problems occurred. A probable reason for the lack of electrolytic corrosion is that the condensate is a poor electrolyte.

Engineering Results

The ratio of overall heat-transfer coefficients for dropwise (gold-plated) vs. filmwise (uncoated) condensation is dependent on many factors. For example, the ratio increases with increasing velocity of cooling water and with the use of substrate materials of higher thermal conductivity. The ratio also increases with inundation. (Inundation is the passage of condensed water from the upper tubes in a horizontal tube bundle over the lower tubes.) In a laboratory experiment with the gold-silver-nickel system at cooling water velocity of 183 cm/sec, the ratio was 1.40 with no overhead tubes and 1.66 at 60 equivalent overhead tubes. At 366 cm/sec coolant flow, the ratio was 1.67 with no overhead tubes and 2.31 at 60 overhead tubes. The integrated ratio for a 60-tube bundle at 183 cm/sec is 1.58 and at 366 cm/sec is 2.11. This corresponds to a 58 per cent and 111 per cent increase in overall coefficients. For the lower velocity a plant normally requiring 1000 km of tubes, would require only 632 km of the gold-coated tubes. For the higher velocity, only 474 km of gold-coated tubing would be needed to do the job of 1000 km of ordinary tubing.

Laboratory studies of possible contamination of tubes by wettable oxides from nearby copper or iron surfaces have indicated that iron rust is potentially a severe contaminant and can adhere to the gold surface to cause filmwise condensation. This may require steps to be taken in design of plants for dropwise condensation, to prevent rust particles from being carried to the surfaces entrained in droplets in the steam, by means of appropriate baffles, demisting screens and overall geometry. Also no iron contamination from the overhead shell must reach the tube bundle.

Contamination was encountered initially in the first larger-scale test, with a 'satellite' plant containing 20 gold-plated horizontal tubes (1.59 cm diameter, 103 cm long) using sea-water steam from Stage 16 of the Clair Engle Test Bed Plant at the San Diego Test Facility of the Office of Saline Water. Figure 2 shows the satellite plant at the time of installation. The first test was discontinued after 8 weeks of operation with most of the tubes seriously stained and filmwise. One problem related to the tubes themselves; these had not been plated by the now-recommended procedure and had a rough (non-specular) finish, which tended to hold particulate contaminants. New gold-silver-nickel-coated tubes with a specular finish were prepared. The other problem, that of wettable particulates entrained in the steam, was attacked by putting a demisting screen



A satellite plant (upper centre) used for condensation studies on gold-plated tubes at the Clair Engle Test Bed Plant of the Office of Saline Water. This contained twenty horizontal tubes using sea-water steam

in the steam line. The performance improved significantly after these changes and in the initial period of operation of 1615 hours all tubes produced excellent dropwise condensation. Intermittent operation of the plant since then has caused problems in evaluation of long-term dropwise behaviour, though at last report the heat transfer coefficients continued significantly higher than those for the filmwise parent plant.

Another plant test to be under way is with a vertical-tube still at the O.S.W. Wrightsville Beach Test Facility. Figure 3 illustrates gold-plated and parylene-coated tubes to be tested (nine of each). Parylene is a vapour-deposited p-xylylene polymer (Union Carbide); the electrodeposited gold dropwise systems have longer lives and higher heat transfer coefficients than the parylene coatings. Other tests with long, vertical, gold-plated tubes (6m) with vortex-flow are being conducted by Dr Hugo Sephton of the University of California at Berkeley.

Potential Applications and Steps to Further Development

All the research on gold dropwise-condensing systems to date has dealt with the application in desalination, aimed toward reducing costs of large sea-water distillation plants using conventional tubing materials. Other applications have the potential either of significant cost savings and/or other benefits. For example:

(1) In smaller distillation systems—such as shipboard stills—where there is a much greater installed cost per unit area of condenser than for the large land-based plants, the dropwise systems could produce great cost savings.

(2) In any sea-water distillation plants in which a more expensive tube material—such as titanium—is used, the permanent dropwise systems could lead to even greater cost savings than with equivalent-size conventional plants.

(3) In certain cases—as with deep-submersible naval vessels—the reduction in size and weight of power-plant or other condensers could be of very great benefit.

(4) In land-based power plants the gold-plated dropwise systems could not only reduce the size of the condenser system but also reduce significantly the amount of copper oxides and other materials from tube erosion which can become entrained in the steam to give rise to harmful deposits on the turbine blades.

(5) With aluminium condenser tubes (and this should be considered in the light of their potential use in sea-water distillation plants) steam-side corrosion could be eliminated by the use of the noble-metal dropwise coatings typified by the gold-silver-nickel (Alstan 70) system.

Further steps need to be taken to develop the potential of the gold dropwise systems. These steps include:

(1) Engineering studies—particularly heat-transfer measurements under various conditions (temperature differences between steam and cooling water, steam

Tubes coated with gold and with p-xylylene polymer for tests in a vertical tube still at the Wrightsville Beach Test Facility of the Office of Saline Water

velocities, presence of non-condensable gases, etc.)—to be used as inputs for design of systems to utilise the dropwise condensation.

(2) Design of plants, small and large, specifically for dropwise condensation; for example, with high coolant velocities and with special provisions for preventing contamination (e.g., plastic linings for steel shells).

(3) Development of automated electrodeposition processes for quantities of very long tubes, for example, 20 metres.

(4) Operating prototype plants with gold-plated tubes for a number of years to establish the proven reliability of performance needed for commercial use.

We have in dropwise condensation a new and different use for gold, one which should some day have great usefulness in the area of heat transfer. To bring it from the laboratory scale to large-scale application will require much additional effort, but this effort should be rewarded with a significant advance in technology—one which is based on the unique properties of gold.

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Laser-modified Gold Films

Intense laser beams may damage optical instruments if they are not protected from the radiation. A protective technique in which thin gold films were vapour deposited on to quartz blanks has been investigated by P. D. Poulsen of General Dynamics, San Diego, California (*Appl. Optics*, 1972, **11**, (4), 949). Coatings with about 30 per cent peak transmittance at 0.5 μm were able to withstand 10.6 μm radiation from an 80 watt carbon dioxide laser focused on to a 3 mm spot (1.2 kW/cm^2) for several minutes, whereas an unprotected quartz surface was damaged in less than one second.

Furthermore, the reflectance was improved by this irradiation, presumably by melting of surface gold particles to form a smooth surface. At the same time the transmittance was also increased in the visible region. When the gold film was removed from the quartz, both adherence and apparent hardness of the coating were found to have been enhanced by the irradiation. However, thicker opaque gold films did not show such enhanced reflectance.