Solubility of Cupric Oxide in Pure Subcritical and Supercritical Water

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The solubility of cupric oxide in pure water has been measured over the temperature range 50° to 550° C. along a series of isobars between 3500 and 6000 p.s.i.g., using a continuous flow method. The results show an increase of solubility with temperature up to a maximum of 855 μg. of Cu per kg. at approximately 320° C.; with further increase of temperature, the isobaric solubility decreases to a minimum, the temperature and solubility level of which is dependent on pressure. These measurements represent the first comprehensive study of the solubility diagram of cupric oxide, which is qualitatively similar to that of silica and germanium dioxide.

THE DISSOLUTION, transport, and deposition of metallic oxides is an important factor in the operation of the high-pressure water circuit of modern power station boiler units. As feedwater purity improves, the relative importance of the metallic oxide impurities, which result largely from the corrosion of the water circuit containment itself, increases.

A major parameter in each of the processes quoted above is the solubility of the oxide species in the high-temperature, high-pressure aqueous environment, but there is little data available for the systems of greatest practical significance, Fe_3O_4-H_2O, CuO-H_2O, and Cu_2O-H_2O. Sweeton *et al.* (*8*, *9*) have studied the subcritical solubility of magnetite, Fe_3O_4, as a function of chloride ion concentration, while a small area of the supercritical solubility diagram for the system Fe_3O_4-H_2O has been explored by Martynova (*6*). The measurements made by Pocock and Stewart (*7*) in the systems Cu-H_2O, Cu_2O-H_2O, and CuO-H_2O were over a restricted range of pressure and temperature, and the results showed considerable scatter.

In the present work, the solubility of cupric oxide, CuO, has been measured in pure water of pH 7.5 over the temperature range 50° to 550° C. and along a series of isobars between 3500 and 6000 p.s.i.g.

EXPERIMENTAL

Apparatus. A schematic diagram of the apparatus is shown in Figure 1. Distilled, deionized make-up water is deaerated before being fed to the main high-pressure pump, which is a reciprocating type with an infinitely variable stroke rated at 10,000 p.s.i.g., 22 kg. of water per hour. The boiler consists of approximately 30 meters of 14-mm. o.d., 5-mm. i.d. nimonic 80A tubing (Table I), which is itself utilized as the low-voltage heating element. A further 6 meters of identical tubing forms the superheater, in which fine control of the water temperature is achieved, using a three-term controller.

The water temperature at the inlet to the air furnace is maintained at the desired temperature by the line heaters,

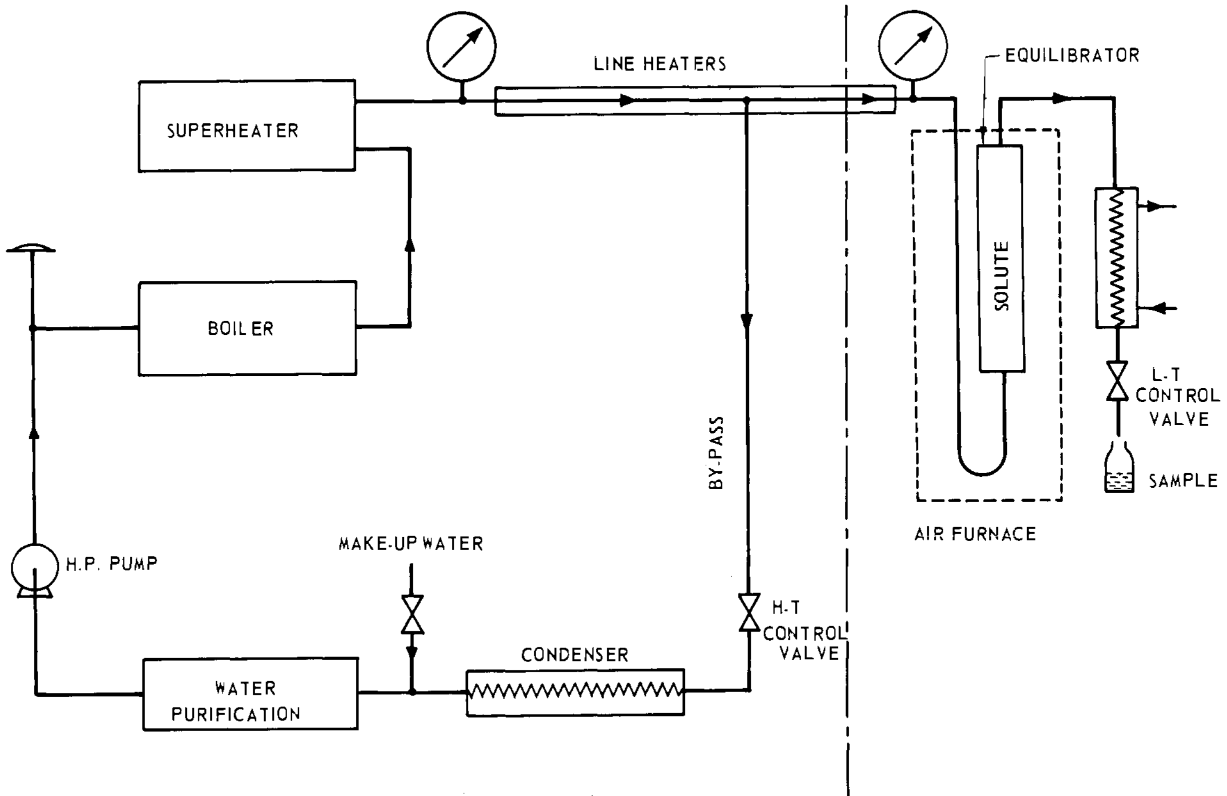


Figure 1. Solubility apparatus

Table I. Alloy Composition, %

	80A	90
Carbon	0.1	0.13
Silicon	1.0	1.5
Iron	5.0	5.0
Manganese	1.0	1.0
Chromium	18-21	18-21
Titanium	1.8-2.7	1.8-3.0
Aluminum	0.5-1.8	0.8-2.0
Cobalt	2.0	15-21
Nickel	Balance	Balance

while the air furnace, which contains the equilibrator and sample, is controlled at the same temperature. In operation, the three controlled temperatures, that is, superheater outlet water, air furnace inlet water, and air furnace, are maintained to ±1° C. The water temperature at the inlet and outlet of the air furnace is measured by chromel-alumel thermocouples, which are accurate to within ±0.11° C. of the British Standard thermocouple tables, and recorded to an accuracy of ±0.5° C.

Approximately 500 grams of cupric oxide, in the form of 1-mm. diameter oxidized copper wire, is contained within the nimonic 90 (Table I) equilibrator by 125-mesh stainless steel gauze, giving a bed depth of 20 cm. The geometric surface area of this charge is of the order of 25,000 $cm.^2$.

The pressure in the system is controlled by manual adjustment of the two control valves, shown in Figure 1, to an accuracy of ±50 p.s.i. During each experimental run, the pressure at the inlet to the air furnace is measured with a calibrated dead-weight piston gage to an absolute accuracy of ±15 p.s.i.

The mass flow rate of water through the boiler unit is controlled by the length of the high-pressure pump stroke, while the proportion of the total flow passing through the equilibrator is determined by the settings of the two control valves and is measured at the sample outlet to an accuracy of ±0.06 kg. per hour. During an experimental run, flow rate variations could be up to 1 kg. per hour.

Experimental Procedure. After loading the equilibrator with a fresh sample of cupric oxide, the bed was flushed with cold water at a high flow rate to remove any fine particles of oxide that might be carried into the sample stream.

At the start of a series of experiments, the system was heated to the desired temperature with the low-temperature control valve closed; that is, no flow through the equilibrator. Once at temperature, the control valves were adjusted to give the required pressure and sample flow rate. Thereafter, experimental conditions were altered without interrupting the sample flow.

On shut-down, the low-temperature valve was closed and the heat load reduced in stages to give a gradual reduction in temperature, thereby minimizing thermal shock to the system. The high-temperature control valve was closed and the high-pressure pump stopped when the superheater outlet temperature fell below 100° C. When shut down, the system remained full of water, under pressure.

Sampling and Analysis. For the first measurement of a series, the experimental conditions were held steady for about 30 minutes before the sample was taken. Subsequently, samples were taken after conditions had remained steady for 10 to 15 minutes following a change in temperature or pressure. If the temperature varied by more than ±2° C. or the pressure by more than 150 p.s.i. during the period of sample collection, the sample was rejected.

The time for the collection of a sample depended solely on the flow rate through the equilibrator, since the sample volume, 450 ml., was fixed by the requirements of the analytical method. Each sample was collected in an acid-cleaned polyethylene bottle which contained 10 ml. of 5*N* hydrochloric acid to ensure that the dissolved copper oxide remained in solution. The analytical method used was developed by Wilson (*10*) for the concentration range 0 to 50 μg. of Cu per kg. and has, over this range, a total standard deviation of 0.15 to 0.7 μg. of Cu per kg. Extension of this method to the copper levels encountered in this study involves a dilution procedure which increases the analytical error. The standard errors quoted in Table II take account of dilution as necessary. Repeat determinations on a given sample agreed to within the error limits quoted.

The flow rate through the solute bed was measured immediately before and after sampling, while the temperature and pressure were measured at one-minute intervals during sampling.

RESULTS

Table II lists the measured solubilities of cupric oxide and the pertinent conditions of temperature, pressure, and mass flow rate. The basis on which the errors given in Table II were estimated are: solubility, the analytical error to 95% confidence limits, pressure and temperature, combination of in-run variation and errors in measurement, and mass flow rate, half the difference between the two measurements.

In the superpressed water region, below 320° C., variation of the pressure, in the range 2000 to 6000 p.s.i.g., had no significant effect on the measured copper concentration.

Initially, in the absence of a cupric oxide sample, blank runs were made under various temperature and pressure conditions; the measured iron and copper concentrations at the sample outlet did not exceed 3.0 μg. per kg.

At the conclusion of a series of experiments, x-ray powder photographs of the cupric oxide sample showed no evidence of reduction to cuprous oxide.

Effect of Flow Rate Variation. No dependence of the measured copper concentration on the flow rate was found at any temperature; it was assumed, therefore, that the solution leaving the equilibrator was saturated. With a sample of 500 grams, the residence times of the water within the packed bed of oxide ranged from 4.5 to 540 seconds, depending on the flow rate, temperature, and pressure. Typical examples of measurements of the effect of flow rate are given in Table III.

Carryover. Continuous flow methods for determining solubilities are subject to the possibility that particulate solute may be carried over with the sample. Experiments to determine the carryover during sampling by dividing the sample flow into a filtered (0.1-micron millipore) and unfiltered stream showed that no significant carryover occurred.

Reproducibility of Measurements. Solubility measurements obtained using the experimental procedure described above, under similar conditions but at different times, showed good agreement; for example, the three measurements detailed in Table II at 260° C. were taken over a period of three months. Moreover, the results obtained during normal operations gave a self-consistent solubility diagram, as demonstrated by Figure 2.

The short-term reproducibility is illustrated by the value of 610 ± 32 μg. of Cu per kg. quoted for 322° C., which is the average of six samples taken consecutively under steady operating conditions.

Deposition. In all solubility determinations involving the cold sampling of high-temperature, high-pressure solutions in systems with a positive temperature coefficient of solubility, deposition is a major problem. In the present study, deposition began in the line connecting the air furnace outlet to the high-pressure condenser, but the bulk of the deposit occurred in the condenser and the low-temperature valve. Figure 2 demonstrates that the temperature at which the solution produced in the equilibrator supersaturates

Table II. Solubility of Cupric Oxide in Water

Temp., ° C.	Pressure, Lb./In.^{2} Gage	Mass Flow Rate, Kg./Hr.	Sol., μG. of Cu/Kg.
57 ± 1	1730 ± 25	8.0 ± 0.7	12.4 ± 0.3
69 ± 2	1200 ± 100	1.4 ± 0.2	16 ± 2
81 ± 2	1100 ± 100	4.0 ± 0.3	23 ± 2
87 ± 2	3830 ± 25	2.6 ± 0.1	23.5 ± 1
88 ± 1	3850 ± 15	5.9 ± 0.1	21.5 ± 1
89 ± 1	3950 ± 75	3.8 ± 0.2	17 ± 1
110 ± 2	3300 ± 80	0.8 ± 0.1	23.5 ± 1
117 ± 2	3700 ± 45	4.3 ± 0.05	29 ± 1
121 ± 2	3520 ± 40	2.4 ± 0.05	38 ± 1
122 ± 3	3450 ± 65	6.7 ± 0.1	23 ± 1
133 ± 2	1200 ± 100	4.2 ± 0.1	26 ± 1
154 ± 2	1200 ± 100	5.5 ± 0.1	52 ± 2
181 ± 2	2640 ± 35	2.1 ± 0.1	198 ± 5
187 ± 1	2005 ± 20	3.5 ± 0.2	143 ± 3
207 ± 3	1900 ± 100	4.7 ± 0.1	212 ± 2
232 ± 1	3025 ± 30	5.1 ± 0.1	281 ± 5
234 ± 2	3870 ± 45	6.4 ± 0.1	289 ± 6
249 ± 2	2900 ± 100	6.0 ± 0.3	360 ± 4
252 ± 1	3020 ± 35	5.5 ± 0.1	391 ± 5
260 ± 1	3780 ± 55	6.9 ± 0.5	393 ± 7
260 ± 1	3900 ± 115	7.2 ± 0.1	378 ± 8
260 ± 2	4135 ± 30	8.7 ± 0.1	395 ± 5
273 ± 2	3200 ± 50	7.3 ± 0.1	444 ± 10
291 ± 1	4055 ± 20	9.0 ± 0.1	503 ± 5
298 ± 2	3225 ± 50	8.7 ± 0.1	516 ± 6
307 ± 2	4200 ± 100	3.0 ± 0.9	547 ± 10
322 ± 3	3270 ± 40	3.8 ± 0.5	610 ± 32
331 ± 2	4200 ± 35	10.6 ± 0.1	600 ± 6
350 ± 1	4000 ± 65	6.6 ± 0.1	462 ± 10
350 ± 1	6000 ± 65	8.6 ± 0.2	570 ± 10
374 ± 4	3500 ± 65	6.0 ± 0.2	234 ± 10
379 ± 2	3950 ± 100	2.0 ± 0.2	137 ± 6
376 ± 2	4000 ± 100	3.0 ± 0.2	194 ± 6
389 ± 1	4055 ± 15	6.9 ± 0.2	233 ± 8
389 ± 1	3995 ± 20	6.5 ± 0.1	227 ± 8
381 ± 2	4000 ± 65	5.0 ± 0.2	331 ± 10
378 ± 2	4500 ± 65	9.1 ± 0.3	337 ± 10
381 ± 2	5000 ± 65	8.1 ± 0.1	320 ± 10
381 ± 2	5500 ± 65	8.7 ± 0.3	350 ± 10
382 ± 2	6000 ± 65	7.0 ± 0.1	486 ± 10
386 ± 2	4050 ± 100	5.8 ± 0.2	89 ± 6
388 ± 2	4600 ± 100	3.2 ± 0.2	151 ± 6
401 ± 1	4305 ± 20	9.3 ± 0.2	117 ± 1
408 ± 2	4925 ± 40	9.9 ± 0.6	129 ± 1
401 ± 3	5100 ± 100	4.4	170 ± 1
401 ± 2	5000 ± 65	4.4	182 ± 1
405 ± 1	5375 ± 30	9.5 ± 0.1	214 ± 1
405 ± 1	6070 ± 25	12.0 ± 0.2	406 ± 6
420 ± 2	3840 ± 60	7.7 ± 0.1	46 ± 1
422 ± 1	4035 ± 50	10.9 ± 0.3	90 ± 1
421 ± 2	4435 ± 50	9.6 ± 0.2	64 ± 1
440 ± 2	4970 ± 65	10.2 ± 0.2	92 ± 1
430 ± 1	5060 ± 45	11.5 ± 0.5	100 ± 1
431 ± 2	5500 ± 65	9.9 ± 0.1	153 ± 2
434 ± 2	6000 ± 130	7.2 ± 0.3	315 ± 5
440 ± 1	3455 ± 30	8.4 ± 0.4	77 ± 1
448 ± 2	5990 ± 105	5.6 ± 0.6	299 ± 2
460 ± 2	3500 ± 80	4.0 ± 0.3	56 ± 1
460 ± 1	3500 ± 65	6.9 ± 0.3	81 ± 1
455 ± 2	4010 ± 75	8.4 ± 0.1	101 ± 1
469 ± 2	4520 ± 65	5.7 ± 0.2	80 ± 1
468 ± 2	5060 ± 45	5.5 ± 0.1	108 ± 2
463 ± 2	5490 ± 75	7.4 ± 0.3	139 ± 4
462 ± 2	6000 ± 115	6.4 ± 0.4	126 ± 4
461 ± 2	6050 ± 70	2.7 ± 0.3	184 ± 6
497 ± 1	3465 ± 50	7.7 ± 0.4	113 ± 1
497 ± 1	4065 ± 25	8.6 ± 0.1	121 ± 1
502 ± 1	4465 ± 40	9.5 ± 0.4	145 ± 1
501 ± 2	5045 ± 30	8.8 ± 0.4	148 ± 1
500 ± 2	5425 ± 40	6.0 ± 0.1	138 ± 2
503 ± 2	5980 ± 95	8.2 ± 0.1	178 ± 2
550 ± 1	3530 ± 45	7.8 ± 0.1	115 ± 1
550 ± 1	4050 ± 35	6.7 ± 0.1	100 ± 1
551 ± 2	4575 ± 35	9.3 ± 0.3	133 ± 1
551 ± 1	5050 ± 40	8.6 ± 0.1	165 ± 1
550 ± 1	5510 ± 35	8.7 ± 0.1	172 ± 2
550 ± 1	5980 ± 40	6.8 ± 0.1	159 ± 2

in the cooling system depends on the temperature and pressure within the equilibrator. Thus, for

(a) temperatures up to approximately 320° C., supersaturation occurs as soon as cooling commences.

(b) temperatures between 320° C. and the temperature of the solubility minimum on a given isobar, cooling at first desaturates the solution, which does not resaturate until the temperature of equivalent solubility in region (a) is reached.

(c) temperatures above that of minimum solubility, the solution is supersaturated until the temperature of equivalent solubility in region (b) is reached; thereafter, the behavior is as described for (b) above.

The rate of deposition at a given point in the cooling system depends primarily on the temperature and degree of supersaturation at that point. Moreover, deposition is influenced by other factors, such as the nature of the substrate; thus, it is extremely difficult to estimate the amount of deposition in a given experiment. The rate of deposition, or proportion of dissolved copper deposited from solution, increased with time under steady operating conditions. For example, Figure 3 shows the result of two experiments at 250° C. where the conditions were held constant for approximately 5 hours. The average concentration of copper in the bulk sample was 275 ± 7 and 256 ± 10 μg. of Cu per kg., respectively, while the total deposited copper, found by cleaning the sampling system before and after each experiment with 2*N* nitric acid, was equivalent to 91 ± 3 and 121 ± 5 μg. of Cu per kg. in the two cases. Addition of the solution sampled and deposited copper gives solubility values of 366 ± 10 and 377 ± 15 μg. of Cu per kg., which are experimentally the same as both the concentration in the long-term runs at time zero (367 ± 15 μg. of Cu per kg.) and the solubility value for 249° C. quoted in Table II (360 ± 4 μg. of Cu per kg.).

Table III. Typical Examples of the Flow Rate Effect

Temp., ° C.	Pressure, Lb./In.^{2} Gage	Mass Flow Rate, Kg./Hr	Contact Time, Sec.	Concn., μG. of Cu/Kg.
401 ± 1	4305 ± 20	9.3 ± 0.2	16	117 ± 1
401 ± 2	4235 ± 50	4.4 ± 0.2	34	118 ± 1
122 ± 3	3450 ± 65	6.7 ± 0.1	64	23 ± 1
120 ± 2	3300 ± 80	0.8 ± 0.1	535	23.5 ± 1
88 ± 1	3850 ± 15	5.9 ± 0.1	76	21.5 ± 1
89 ± 1	3950 ± 75	3.8 ± 0.2	115	17.5 ± 1
87 ± 2	3830 ± 25	2.6 ± 0.1	170	23.5 ± 1

At the highest solubility values, the equivalence of concentration at establishment of steady operating conditions and solubility does not hold; that is to say, deposition is significant at all times in this case. The values obtained for the maximum solubility using the short-term experimental technique were of the order of 600 μg. of Cu per kg., but using the long-term method employing acid-cleaning for removal of deposited copper and copper oxides, the value obtained was 855 ± 30 μg. of Cu per kg. at 319° ± 1° C., 2425 ± 10 p.s.i.g., 4.5 ± 0.5 kg. per hour.

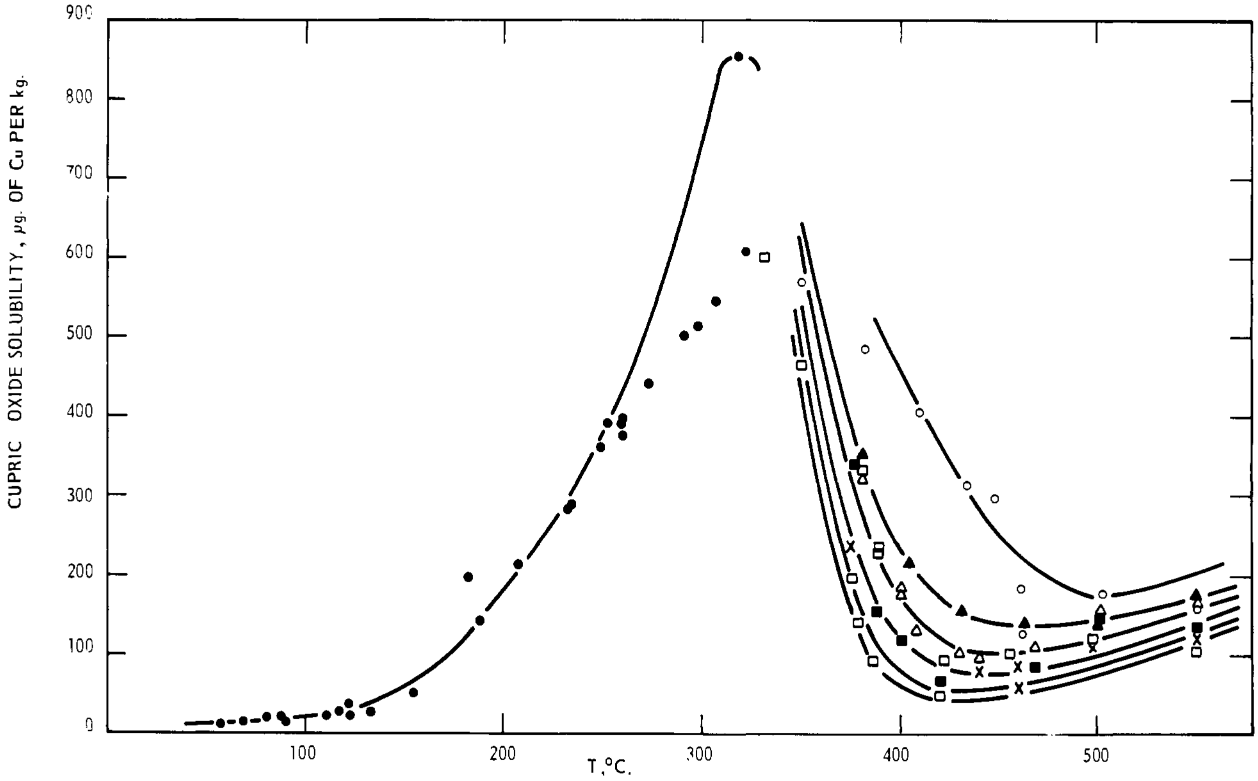


Figure 2. Solubility of cupric oxide in pure water

● Superpressed water
○ 6000 p.s.i.g.
▲ 5500 p.s.i.g.
△ 5000 p.s.i.g.
■ 4500 p.s.i.g.
□ 4000 p.s.i.g.
X 3500 p.s.i.g.

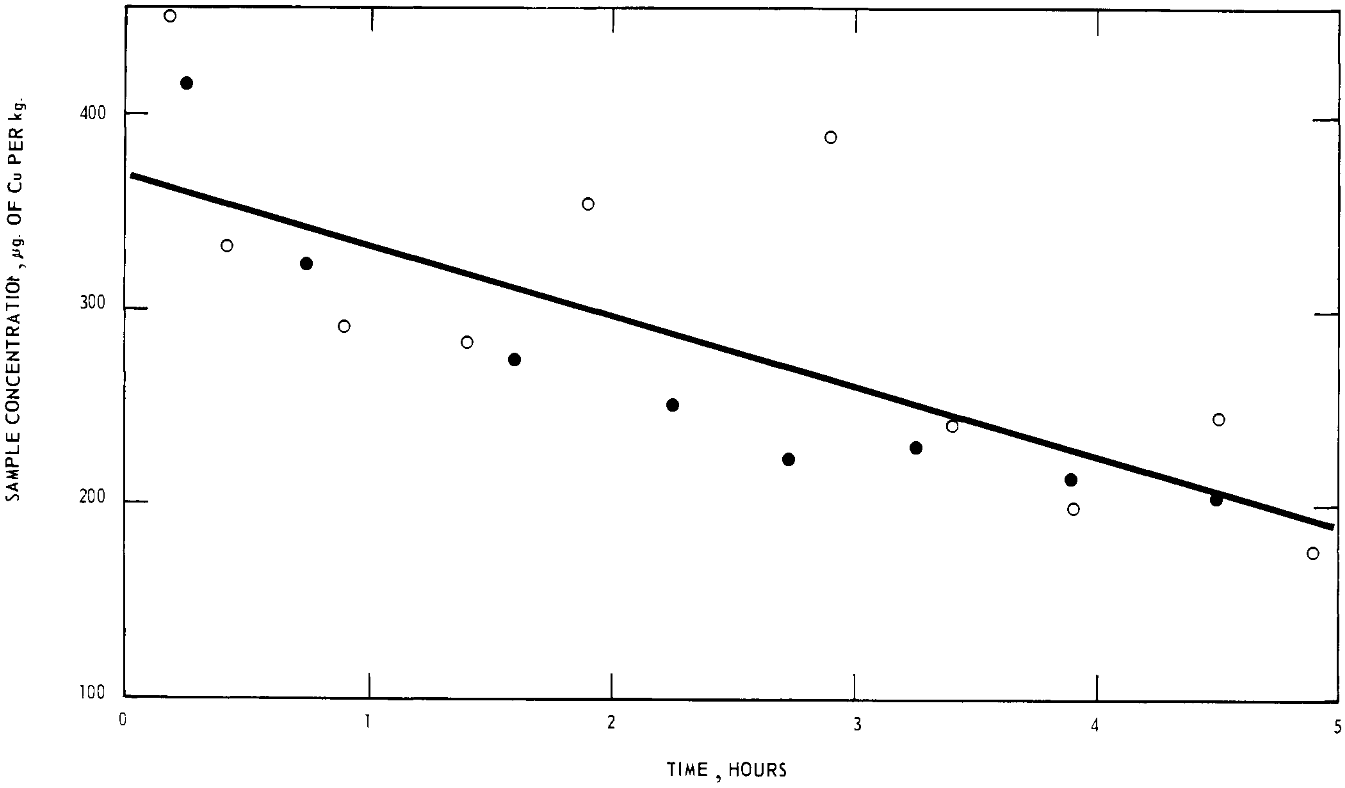


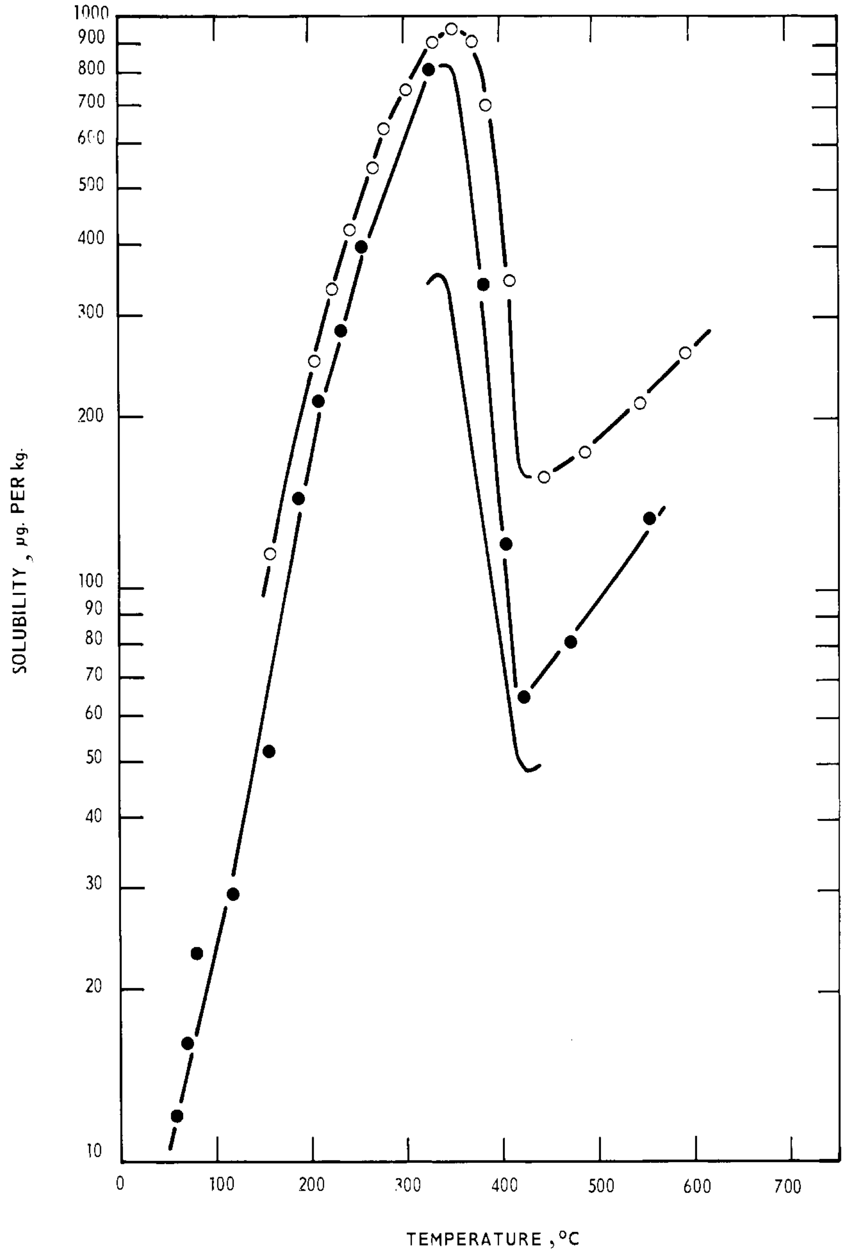
Figure 3. Variation of measured copper concentration with time under steady operating conditions

○ Run A: 251 ± 2° C., 4000 ± 200 p.s.i.g.
● Run B: 251 ± 1° C., 4000 ± 50 p.s.i.g.

Figure 4. Isobaric solubility of CuO, SiO_2, and GeO_2 in water

● Present results, CuO, 4500 p.s.i.a.

○ Heitmann (*4*), SiO_2 (quartz), 4485 p.s.i.a. x 10^{-3} Interpolated from Glemser *et al.* (*2*), GeO_2, 4485 x 10^{-4} p.s.i.a.



It was assumed that solubility values of lower absolute value than 360 µg. of Cu per kg. obtained by the short-term method of operation are valid, while those above 360 µg. of Cu per kg. are subject to error due to deposition, which is proportional to the solubility and rises from zero at approximately 400 µg. of Cu per kg. to a maximum of 230 µg. of Cu per kg. at the solubility maximum. Figure 2 shows the solubility diagram obtained when the data of Table II are modified by the error due to deposition.

DISCUSSION

Comparison of the solubility values reported here with those previously reported (*7*) under similar conditions of temperature and pressure show that the latter values are much lower, in some cases by an order of magnitude. The reason for this discrepancy cannot be positively ascertained, but three aspects of the work of Pocock and Stewart deserve comment.

Corrosion of their stainless steel water circuit was directly visible, and was confirmed by the analysis of hydrogen at the control valve. In the majority of their experiments, the ratio of iron to copper concentrations found in the samples was close to unity and it is possible, therefore, that the measured copper concentration was modified by the formation of compounds such as delafossite, $CuFeO_2$, which is a frequent component of boiler and turbine oxide deposits (*5*).

When using a packed bed of solute, the steam-solute contact time is essentially equal to the steam residence time within the equilibrator, but this will not necessarily be true of the configuration used by Pocock and Stewart. Hence, while the residence time of the steam within the equilibration autoclave used by Pocock and Stewart was of the same order as that used in the present work (approximately two minutes), it is possible, in the absence of specific experiments to prove the contrary, that the solutions leaving their equilibrator were not saturated with solute.

Modification of the apparatus described here to include a back-pressure regulator and a recording flow meter necessitated the use of stainless steel components and, even at low temperature, the soluble copper plates out on the stainless steel—probably by an electrochemical displacement reaction—as copper metal, thereby giving low solubility values. The plated copper, in contrast to that deposited from supersaturated solution, largely as the oxide, is difficult to remove by flushing with 2*N* nitric acid. Since the Pocock and Stewart equipment was constructed of stainless steel, this plating process probably occurred at all points downstream of their equilibrator, and may well have contributed significantly to the low solubility values that they reported.

The solubility diagram of cupric oxide obtained in this work is qualitatively similar to that of silica (*4*) and germanium dioxide (*2*), as shown by Figure 4 (*3*). This similarity suggests that the type of solubility equation proposed by Frank (*1*), Martynova (*6*), and others is generally applicable to aqueous high-temperature metal oxide solubilities. The equations are of the basic form

$$\log S = A - \frac{B}{T} - n \log V$$

where S is the solubility, T is the temperature in °K., n is the hydration number of the solvated solute, V is the specific volume of the solvent, and A and B are constants. They are derived from the initial assumption that the solute exists in solution as un-ionized molecules hydrated with an average number, n, of solvent molecules. The experimental results can be described by this equation over a limited temperature range above the critical temperature, but not over the whole temperature range. While it is likely that at supercritical temperatures un-ionized molecules may be in solution, at lower temperatures, where the dielectric constant of water is high, copper ions probably exist in solution, and a more complex equilibrium situation would occur, one that would not be described by the above equation.

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Phase Equilibria in Hydrocarbon Systems

Volumetric Behavior in the Methane–Propane–*n*-Decane System

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The results of an experimental investigation of the volumetric behavior of 22 mixtures of methane, propane, and *n*-decane are reported. The experimental measurements were carried out at pressures between 200 and 10,000 p.s.i. in the temperature interval between 40° and 460° F. Some 5500 states were investigated. The compositions of the mixtures studied were selected to permit the direct evaluation of the partial volumetric behavior of each of the components.

THE VOLUMETRIC behavior of ternary hydrocarbon mixtures has not been investigated extensively. The only experimental investigation known to the authors, covering a wide range of pressures and temperatures, is a study of the volumetric behavior of the methane–*n*-butane–*n*-decane system (*7, 8, 10, 12, 13*). Studies of the volumetric behavior of binary hydrocarbon systems are more extensive. Examples of related binary systems include the methane-propane (*11*), methane-decane (*9, 19*) and propane-*n*-decane (*3, 15*) systems. In addition, five of the binary systems associated with the quaternary system, methane–propane–*n*-butane–*n*-decane, have been investigated throughout the pressure interval between 200 and 10,000 p.s.i. at temperatures between 40° and 460° F.

To complete a study of a second ternary system of the quaternary system, methane–propane–*n*-butane–*n*-decane, an investigation of the volumetric and phase behavior of the methane–propane–*n*-decane system was undertaken. The results of the phase behavior measurements are available (*20*). The data presented earlier (*20*) include the volumetric behavior of the coexisting liquid phase. These latter data were based upon the volumetric measurements reported here.

A systematic study of 22 mixtures of methane, propane, and *n*-decane was carried out at pressures between 200 and 10,000 p.s.i. and at eight temperatures between 40° and 460° F. The compositions investigated are shown in Figure 1 and recorded in Table I. These compositions were so chosen as to permit each composition to fall at the intersection of three straight lines representing fixed ratios of the mole fractions of each of three pairs of the components. For example, the line AB in Figure 1 represents a ratio of the mole fraction of propane to the sum of the mole fractions of *n*-decane and propane of 0.6806. The choice of compositions was made to yield fixed values of the following composition parameters.

$$C_{3,10} = \underset{\bullet}{x}_3/(\underset{\bullet}{x}_3 + \underset{\bullet}{x}_{10}) \qquad (1)$$

$$C_{10,1} = \underset{\bullet}{x}_{10}/(\underset{\bullet}{x}_{10} + \underset{\bullet}{x}_1) \qquad (2)$$

$$C_{1,3} = \underset{\bullet}{x}_1/(\underset{\bullet}{x}_1 + \underset{\bullet}{x}_3) \qquad (3)$$