

Deposits Formed Beneath Bubbles During Nucleate Boiling of Radioactive Calcium Sulfate Solutions

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Moore and Mesler postulated microlayer evaporation beneath a bubble to explain the sudden temperature drops observed by them during nucleate boiling of water.

A method was devised to estimate the microlayer thickness from the deposit formed by a series of bubbles during nucleate boiling of saturated calcium sulfate solution containing radioactive sulfur-35. The results support the microlayer evaporation hypothesis.

Moore and Mesler (6) reported rapid drops in surface temperature during nucleate boiling of water. They postulated that the surface was cooled during initial bubble growth by evaporation of a microlayer into the bubble. Rogers and Mesler (8), Hendricks and Sharp (3), Bonnet et al. (1) and Marcus (5) have since obtained support for the microlayer evaporation by determining the relation between bubble growth and surface temperature. This research work was begun to obtain some additional support to this hypothesis by a different method.

In the laboratory it was observed that sometimes deposits form on the boiling surface at the points where bubble columns grow. Closer examination revealed that when solutions were boiled the deposits were circular spots which could have grown from the microlayer depositing its solute each time it evaporated. If so, then it should be possible to determine the microlayer thickness by measuring the mass of the deposit, the number of bubbles grown, and the concentration of solute in the solution. This assumes that the deposit stays on the surface and is not redissolved or otherwise removed. If the microlayer thickness obtained agreed with that reported by Moore and Mesler, then this would be support for their hypothesis.

Surface deposits on boiling surface are termed scale. Scale formation can be regarded as one of the serious problems of boiling heat transfer. Almost the only fundamental work on scale is that of Partridge and White (7) and it concerns the formation of calcium sulfate scale only. Partridge proposed a mechanism to explain the origin of rings on the heat transfer surface, based on the local overheating behind the steam bubbles formed. Due to local increase in temperature of the heating surface under the bubble, fast evaporation of solution at the triple interface of heating surface, steam and water would form a deposit. Repetition of this evaporation around the contact area of the bubble would result in formation of additional rings on the heat transfer surface. This deposit would tend to remain on the surface if the solubility decreased with increased temperature, but otherwise would tend to redissolve. Partridge and White also indicated that if the substance deposited has a negative solubility slope, the crystals will tend to grow by contact with supersaturated liquid film at the heating surface. Later, Freeborn and Lewis (2) proposed a dynamic mechanism similar to the theory of Partridge and White to explain the origin of different types of deposits.

For this study calcium sulfate was chosen as the solute for a number of reasons. The fact that calcium sulfate has such a bad reputation as a scale former gives some assurance that deposits would firmly adhere to the surface. The solubility of calcium sulfate decreases with increasing temperature. This property, together with boiling saturated solutions, would minimize the dissolution of the deposit. The use of calcium sulfate furthermore permits the use of radioactive 87-day sulfur-35 to measure the tiny quantity of the deposit. Sulfur-35 is a good choice for a radioactive species since it has only a weak beta, which minimizes handling difficulties.

Radioisotopes have been used before to study deposits on boiling surfaces. Stout (9) used phosphorous-32 to study the accumulation of phosphates on the boiling surface during the phenomenon of sodium phosphate *hide-out*. The phenomenon called *hide-out* consists of the reduction of the concentration of a salt in the boiler water with an increase in load on the boiler.

EXPERIMENTAL EQUIPMENT

The boiling surface was a Chromel P metal strip mounted in bakelite. One quarter-in. diameter copper rods were silver soldered to the 1/4 in. \times 1/16 in. thick \times 1 in. long Chromel P. strip. A metallographic specimen mounting press was used to mount the strip in red colored bakelite at 275°F. and 3,000 lb./sq. in. gauge. The mount was 1.25 in. in diameter and about 1/2 in. in height. The strip was successively polished on 240-, 300-, 400-, and 600-grit polishing papers. Some of the earlier strips were polished up to 0.1 micron γ alumina wheel. But during the later experiments, the sectional area was reduced in the center and the center section was further undercut to increase the likelihood of bubbles forming away

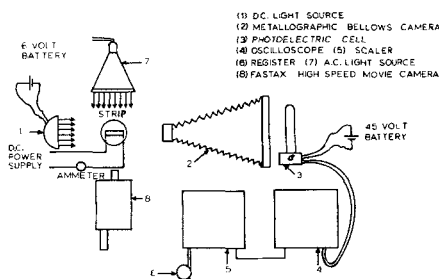


Fig. 1. Schematic diagram of experimental equipment.

TABLE 1. SUMMARY OF RESULTS

Experiment	Number of bubbles (<i>n</i>)	Diameter of deposit (in.)	Contact diameter from high-speed films (in.)	Diameter of spot in autoradiograph (in.)	Microlayer thickness δ ($\times 10^3$ in.)	Corrected microlayer thickness $\delta_{\text{corrected}}$ (10^3 in.)	Estimated† error (percentage)
1	6,632	0.043	—	0.040	49.0	61.7	+150
2	1,766	0.160	—	0.150	89.8	100.5	+150
3	2,631	0.138	—	0.112	30.3	32.0	+200
4	6,514	0.082	—	0.060	17.4	19.0	+300
5	2,856	0.080	0.064	0.060	86.0	103.0	± 20
6	3,229	0.042	0.046	0.034	78.5	99.5	± 20
7	6,473	0.055	0.072	0.060	38.5	45.5	± 20
8	6,492	0.058	0.023	0.026	72.7	102.0	± 20
9	2,623	0.068	0.0227 to 0.0494	0.038	36.5*	40.2*	+200

* Based on 0.0494 in. as contact diameter.

† Estimated error = $\frac{\bar{\delta} - \delta}{\delta} \times 100$. Where $\bar{\delta}$ is the correct microlayer thickness, $\delta = \delta_{\text{corrected}}$.

from the edges. In the latter cases the strips were polished only up to 600-grit polishing paper.

A six-volt D.C. light source 1* was used to illuminate the column of bubbles forming on the strip. An image of the bubbles was obtained in a metallographic bellows camera 2. A 45-volt D.C. supply was connected to an RCA 929 photoelectric cell 3, on which the clear image of the bubbles fell. The output voltage from the photoelectric cell was fed to an oscilloscope 4. The vertical signal from the oscilloscope was fed to a scaler 5 register 6 assembly. The variation of light intensity, caused by the appearance of a bubble, produces an output voltage signal at the photoelectric cell. This signal is amplified several times by the oscilloscope and recorded as one bubble by the scaler register assembly.

A 750-watt A.C. light source 7 was fixed (see Figure 1) to illuminate the bubbles while obtaining high-speed movie pictures with a high-speed movie camera 8 (Fastax high-speed movie camera, WF-17 with a 100-foot film capacity) capable of photographing 4,000 frames per second.

EXPERIMENTAL PROCEDURE

Carrier-free sulfur-35, which is a pure beta radiation source with a half-life of 87.1 days, was used in the form of sulfuric acid in hydrochloric acid solution. Sulfur-35 solution was added to water containing 150% excess of nonradioactive reagent grade calcium sulfate ($\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$) compared to the amount required to make a saturated solution at 100°C. The solution was boiled vigorously under atmospheric pressure in a rectangular tank for about one hour, and allowed to stand at the operating temperature for about six hours to attain equilibrium between radioactive and nonradioactive sulfate ions.

Nucleate boiling experiments were carried out on the Chromel P strip fixed inside the radioactive solution. The heat flux was adjusted so that bubbles were forming at an isolated location away from the edges and the other bubble columns. In many instances an isolated bubble column could not be obtained. The bubbles were counted and on later experiments photographed with a high-speed movie camera once or twice during an experiment. The strip was kept tilted while removing it from the saturated solution so as to minimize drying marks on the strip.

During the initial work of this research with calcium sulfate solutions, it was observed that crystals would grow tremendously if the bubbling rate were slow and if bubbles formed close to each other on the heat transfer surface. The crystal growth was hence minimized by rapid growth of bubbles (more than 10 bubbles/sec.) and by reducing the number of active nuclei on the heat transfer surface.

It was observed that a 1/16 in. thick cardboard sheet could shield all the radiation from a pure beta source. Hence, a

cardboard sheet with a 1/4 in. or 1/8 in. diameter hole punched in the center was used to shield the other unwanted radioactive areas on the strip while counting the radioactivity at the deposit with a Geiger counter.

Kodak type KK x-ray film was used for obtaining autoradiographs of the strips. The autoradiographs revealed distribution of radioactivity around the strips and also showed concentrated spots at the deposits (see Figure 3).

DISCUSSION OF RESULTS

Microlayer thickness, δ , was calculated, assuming that for each bubble a cylinder of solution of diameter, d , and height, δ , evaporates into the bubble; that is

$$(0.7854)(d^2)(2.54)^3(n)(a) = A(c-b)\delta(10^3) \\ \delta = \frac{(c-b)A}{na d^2} (7.76 \times 10^4) \quad (1)$$

The δ thus calculated was corrected for self-absorption of beta rays using Libby's (4) equation. The results of the experiments are tabulated in Table 1. A typical calculation in Appendix I demonstrates the method of computation.

During a preliminary experiment it was observed that after about 25,000 bubbles, part of the deposit came off, possibly because it was too thick. To reduce this possi-

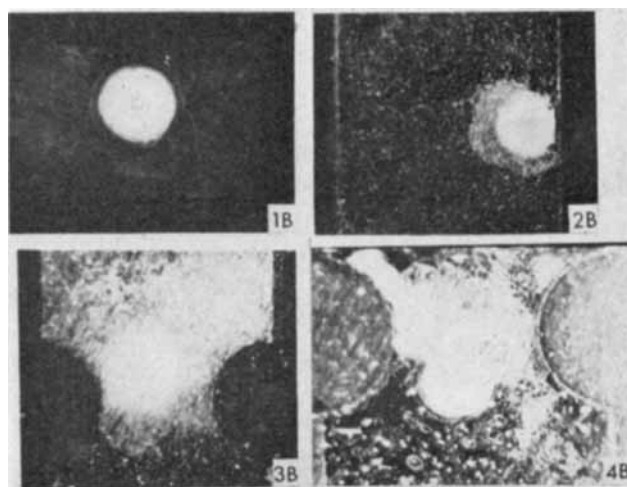


Fig. 2. Calcium sulfate deposits. 1B—experiment 3, 2B—experiment 4, 3B—experiment 7, 4B—experiment 9 (the round deposit in the center). One-quarter in. is the maximum width of strip in each photograph.

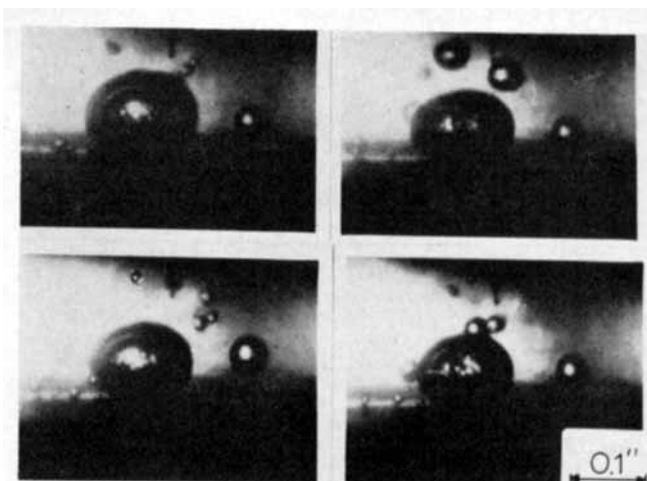
* The underlined numbers refer to numbers in Figure 1.

bility the number of bubbles (hence, the operating time) was reduced to about 7,000. Also, it was found that the deposit, once attached to the surface, could not be washed out easily even by a jet of water. Therefore it has been assumed that once the deposit forms on the surface, it is not removed by the disturbance of bubbles. During the reported experiments no part of any deposit was observed to leave the surface.

High-speed movie pictures were obtained in experiments 5 to 9 to study the relation between the contact diameter of the bubbles and the size of deposit. It was observed that different bubbles grew to almost the same maximum contact diameter (within about 5% variation), except in experiment 9, where there was a wide variation (0.0227 to 0.0494 in.) in the maximum contact diameter from bubble to bubble. Also, it was observed that the maximum contact diameter observed in high-speed movie films was less than the size of the deposit and more than the concentrated spot in the autoradiograph. During the first four experiments the size of the deposit was assumed to be equal to the maximum contact diameter of the bubbles because of lack of high-speed movie film data. Therefore, the calculated microlayer thickness would be less than the actual microlayer thickness.

Bubbles forming just near the edges of strips showed interesting results. The deposit of such bubbles did not reach the edge of the strip (viz., see the deposit in case of experiment 4 in Figure 2). This may be because the edge of the strip is cooled by the conduction of heat to the surrounding bakelite and is thus unable to evaporate as much liquid.

The autoradiographs of the deposits show the relative distribution of the radioactivity in the deposit. The autoradiographs of experiments 5, 6, 7, and 8 showed a uniform concentration over most of the deposit when the autoradiographs were examined with a densitometer (viz., see the deposit of experiment 7 in Figure 3). The high-speed movie films of these experiments also revealed very little variation in the maximum contact diameter (see Figure 4). The uniformity of the deposit revealed by the autoradiographs shows that the microlayer evaporated beneath the bubble is uniform in thickness. In experiment 9, where there was a wide variation of contact diameter from bubble to bubble as seen in the high-speed



film, the autoradiograph (see Figure 3) reveals a less uniform concentration.

The autoradiographs of experiments 1 to 4 showed similar variation of concentration. Hence, the contact diameters of the bubbles may have varied during these experiments. Errors due to variation of contact diameters were estimated based on the maximum size of the deposit in autoradiographs corresponding to big bubbles and the small concentrated spot in the center of the autoradiograph corresponding to small bubbles. It was also assumed that equal number of big and small bubbles formed at the nucleation site. The errors tabulated in Table 1 for experiments 1, 2, 3, 4, and 9 are rather high and the actual errors in these experiments might be much less than the tabulated values.

The deposit of experiment 3 (Figure 2) shows concentric rings similar to the ones reported by Freeborn and Lewis (2) and Partridge and White (7). The autoradiograph of the deposit indicates a concentration at the center but does not show the rings. Unfortunately, high-speed motion pictures were not taken during experiment 3.

Partridge and White (7) proposed that the rings were formed by evaporation at the triple interface where the bubble wall intersects the heating surface. This explanation is quite reasonable. However, the results of these experiments indicate that the evaporation occurring at the triple interface is not significant compared to the evaporation occurring over the entire base of the bubbles. Hendricks and Sharp (3) have arrived at similar conclusions.

Partridge and White further proposed that the rings once formed served as nucleation sites for further deposit of scale. Thus, it might be said that the deposits in these experiments were formed first as ring deposits which filled in their centers. In such a case, the deposit would surely be thickest near the ring. This was not observed. Furthermore, the longest duration of any of the experiments was 3 min. and the bubble frequency was more than 10 bubbles/sec., thus minimizing the opportunity for crystal growth.

The maximum errors involved in computing the microlayer thickness during experiments 5, 6, 7, and 8 were estimated to be $\pm 20\%$, which are due to errors in measurements of the dependent variables, $(c-b)$, n , a , and d only. Variation in the microlayer thickness might be due to heat flux, size of bubble, and frequency of bubble formation—all of which could not be controlled during the experiments.

It was found that microlayer thickness was in the range of 45.5 to 103.0 microinches during experiments 5 to 8, whereas Moore and Mesler (6) have reported microlayer thickness in the range of 78 to 89 microinches. In view of

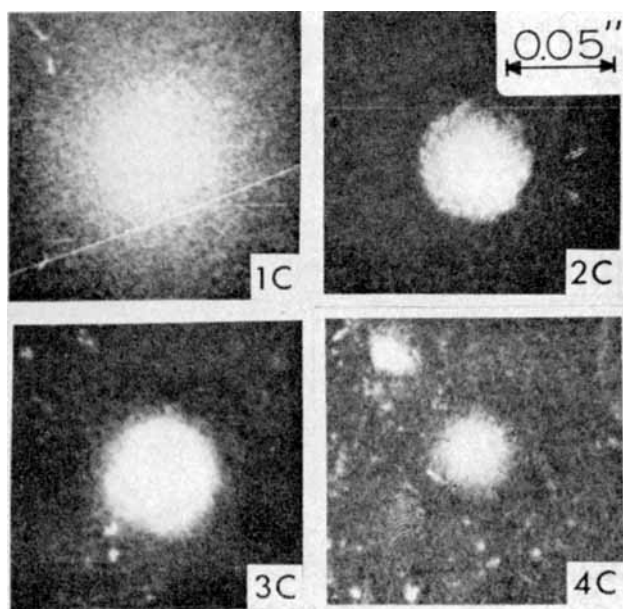


Fig. 3. Autoradiographs of deposits. 1C—experiment 3, 2C—experiment 4, 3C—experiment 7, 4C—experiment 9 (the spot in the center).

the possibility of variation of microlayer thickness with heat flux, rate of bubble growth, size of bubbles, etc., it appears that results of experiments 5 to 8, with minimum errors, are consistent with the values of Moore and Mesler.

CONCLUSIONS

The following conclusions have resulted from this study:

(1) Microlayer thickness can be calculated using a saturated solution of calcium sulfate.

(2) The bubble behavior is consistent with the microlayer vaporization hypothesis forwarded by Moore and Mesler (6). The microlayer thickness computed during this work agrees fairly well with that reported by Moore and Mesler.

(3) The relative distribution of the deposits revealed by the autoradiographs indicates that there is more evaporation beneath the bubble as proposed by Moore and Mesler (6) than there is evaporation at the triple interface as hypothesized by Partridge and White (7).

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NOTATION

- a = radioactivity per ml. of solution at the operating temperature in c.p.m. (counts per minute)
 A = area of the hole in cardboard sheet used in radiation counting in sq. in.
 b = average background radioactivity on the strip in c.p.m./sq. in.
 c = radioactivity at the nucleation site (that is, the deposit) on the strip in c.p.m./sq. in.
 c_o = radioactivity for an infinitely thin layer of deposit in c.p.m./sq. in.
 d = an averaged maximum contact diameter of the bubbles in inches
 I_o = intensity of radiation for infinitely thin layer of S^{35} deposit
 I = intensity of radiation of the sample
 l = density of sample in mg./sq. cm.
 l_n = 15 mg./sq. cm.
 n = number of bubbles
 S = solubility of calcium sulfate at 100°C in g./ml.
 X = l/l_o
 δ = microlayer thickness in microinches
 $\delta_{corrected}$ = microlayer thickness in microinches corrected for self-absorption of beta rays

LITERATURE CITED

- Bonnet, C., E. Macke, and R. Morin, European Atomic Energy Community-EURATOM, EUR 1622f (March, 1964).
- Freeborn, J. and D. Lewis, *Mech. Eng. Sci. J.*, 4, No. 1, 46 (1962).
- Hendricks, R. C. and R. R. Sharp, *NASA Tech. Note NASA TN D-2290* (April, 1964).
- Libby, W. F., *Anal. Chem.*, 19, 2-6 (January, 1947).
- Marcus, B. D., Ph.D. thesis, Cornell Univ., Ithaca, New York (1963).
- Moore, F. D. and R. B. Mesler, *A.I.Ch.E. J.*, 7, 620 (1961).
- Partridge, E. P. and A. H. White, *Ind. Eng. Chem.*, 21, 835-838 (1929).
- Rogers, T. F. and R. B. Mesler, *A.I.Ch.E. J.*, 10, No. 5, 656-660 (1964).

9. Stout, J. W., Jr., *Chem. Eng. Progr. Symposium Ser. No. 39*, 58, 80 (1962).

10. Thorne, P. C. L., and E. R. Roberts, "Ephraim's Inorganic Chemistry," p. 590, Interscience, New York (1948).

APPENDIX I

Typical Calculation For Experiment 3

$$n = 2,631 \text{ bubbles}$$

$(c)(A) = 2114$ c.p.m. with a $\frac{1}{4}$ in. hole in cardboard sheet, that is

$$c = \frac{2114}{(0.7854)(0.25)^2} \text{ c.p.m./sq. in.}$$

Radiation count rate on the entire surface ($5/4$ in. in diameter) was 5,091 c.p.m. on area of $(0.7854)(1.25)^2$ sq. in.

Hence, the average background count rate

$$b = \frac{(\text{count rate on whole strip}) - (\text{count rate at spot})}{(\text{area of the strip}) - (\text{area of the hole in cardboard sheet})}$$

$$= \frac{5091 - 2114}{0.7854 [(1.25)^2 - (0.25)^2]} \text{ c.p.m./sq. in.}$$

Net radiation count rate at nucleation site

$$(c - b) = \frac{2114}{(0.7854)(0.25)^2} - \frac{5091 - 2114}{0.7854 [(1.25)^2 - (0.25)^2]} \text{ c.p.m./sq. in.}$$

that is

$$(c - b)(A) = 2114 - \frac{5091 - 2114}{24} \text{ c.p.m. on a } \frac{1}{4} \text{ in. round area}$$

$$= 1,990 \text{ c.p.m. on a } \frac{1}{4} \text{ in. round area}$$

$$a = 101,875 \text{ c.p.m./ml. of solution}$$

$$d = 0.138 \text{ in. (see Figure 2)}$$

d was assumed to be equal to the size of the deposit in experiments 1 to 4 where high-speed movie data were not available. But in the later experiments d was obtained from high-speed movie films.

From Equation (1) we have

$$\delta = \frac{(c - b)A}{nad^2} (7.76 \times 10^4)$$

Hence

$$\delta = 30.3 \text{ microinches}$$

Correction of δ Due to Self-Absorption of Beta Rays

Libby's (4) equation will be used to calculate self-absorption factor for sulfur-35.

$$l = (S)(n)(\delta)(1000)(2.54 \times 10^{-6}) \text{ mg./sq.m.}$$

where

$$S = \text{solubility of calcium sulfate at } 100^\circ\text{C.}$$

$$= 0.162 \times 10^{-3} \text{ g./ml. (10)}$$

$$X = \frac{l}{l_o} = \frac{l}{15} = (0.274 \times 10^{-6}) n\delta \quad (2)$$

$$\frac{I}{I_o} = \frac{1 - e^{-5x}}{5x} = 0.950, \frac{I_o}{I} = 1.052 \quad (3)$$

$$(c_o)(A) = 1.052(c)(A)$$

$$(c_o \times A) = \frac{(1.052)(2114)}{c_o - b} = 2,230 \text{ c.p.m.}$$

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