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LUCAS HEIGHTS

MASS TRANSFER OF CORROSION PRODUCTS IN HIGH TEMPERATURE, HIGH PRESSURE WATER CIRCUITS

PART 2: PRELIMINARY EXPERIMENTS

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ABSTRACT

The behaviour of iron oxide crud was studied at 25°C and over the range 240 to 270°C in a high pressure water loop. Crud deposition and removal was measured in two parallel, heated Zircaloy-2 tubes using iron-59 as a radioactive tracer. This proved to be a powerful technique capable of detecting crud deposits less than 3 nm thick.

Rapid deposition of crud was observed following injection into the loop of an iron oxide suspension or a ferric nitrate solution. Crud deposited preferentially on heated surfaces when they were present but not to the exclusion of deposition elsewhere; hot spots on heated surfaces attracted additional deposits. Subcooled boiling appeared to be a more important factor than bulk boiling in the enhancement of crud deposition. The initial rapid deposition of the bulk of the crud throughout the loop was usually followed by a slower transfer of crud from other surfaces to any heated surface present.

(Continued)

Unsteady operating conditions, *e.g.* a change in power, temperature or pH, frequently caused crud bursts, but once steady conditions were re-established the entrained crud was quickly redeposited. The bulk of deposited crud was not readily re-entrained, particularly from heated surfaces, so that crud bursts involved only a fraction of the total crud deposited.

Ferric nitrate solutions injected into the loop formed haematite which deposited more slowly and formed more mobile deposits than magnetite which was injected directly into the loop as a slurry. Examination of deposits from both sources showed them to be even and tightly adherent, being removed only with difficulty.

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CORROSION PRODUCTS; DEPOSITION; HIGH PRESSURE; HIGH TEMPERATURE; IRON OXIDES; MASS TRANSFER; MEDIUM TEMPERATURE; PH VALUE; PRIMARY COOLANT CIRCUITS; SUBCOOLED BOILING; WATER

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1. INTRODUCTION

Despite the efforts made to minimise impurities in the cooling water, the deposition of solid metal oxide corrosion products ('crud') onto the surfaces of the coolant circuit still creates problems in modern power plants. In nuclear reactors, crud deposition may threaten the integrity of fuel element cladding [Cartwright *et al.* 1969], restrict coolant flow [Gasparini & Ioannilli 1971], and increase radiation levels around the plant, thereby limiting access and hampering maintenance [Lister *et al.* 1971, Bergmann & Bour 1972].

A large nuclear power plant has an inventory of several hundred kilograms of crud in its primary coolant circuit. The vast bulk of the crud is usually deposited on the surfaces of the system and, under normal steady operating conditions, crud suspended in a circulating coolant is maintained at very low concentrations (typically 1 and 0.01 $\mu g\ g^{-1}$ in Boiling Water and Pressurised Water Reactors (BWR, PWR) respectively) by ion exchange, filtration and blowdown. Following a departure from steady operating conditions - for example after a change in pH or power level - many kilograms of radioactive crud may leave the surfaces rapidly and appear in the coolant, giving rise to the phenomenon known as a 'crud burst'. Crud redeposits rapidly after a crud burst, and only a limited amount is removed by the purification system [Montford 1973]. Thus crud is transferred between in-pile and out-of-pile surfaces by a process of entrainment and deposition.

While crud transfer can be very rapid during crud bursts, the relative infrequency of such bursts limits the total amount of crud transferred in this way. Mass transfer is also important during steady state conditions, when the crud concentration in the coolant is very low, and occurs as a consequence of the very large coolant flowrates [Tomlinson 1973]. For instance, in a typical PWR in which the steady state crud concentration might be 0.01 $\mu g\ g^{-1}$ and the flowrate of the primary coolant about 10^8 kg h^{-1}, crud would be moving around the circuit at 1 kg h^{-1}.

Owing to the large coolant flowrates, the low solubility of iron in water does not preclude the possibility of mass transfer by a solid → solution → precipitation mechanism [Tomlinson 1973]. The low solubility, however, provides an upper limit to the rate of mass transfer *via* solution. For instance, under PWR conditions and using the solubility data of

Sweeton & Baes [1970], the iron transfer *via* solution is limited to 0.6 kg h^{-1}. No such limit exists for particulate transfer.

Although crud mobility is well authenticated, the mechanisms of transfer and deposition remain open to question, largely because of the complexity of the processes involved and the difficulties of experimental investigation. Investigation involves the observation of rapid transfer and deposition of very small amounts of crud (normally encountered in parts per million or less in the fluid and micrometres thick on the surface) in hot, high pressure water systems in which it is difficult to make quantitative measurements. In addition, the crud/surface system is very sensitive to any change in conditions, and the techniques used to measure deposits may affect the process of deposition or the deposits themselves.

The CWL-3 loop was constructed to measure the effects of temperature, pressure, heat transfer, fluid flow and boiling on the deposition and removal of crud under conditions broadly similar to those found in nuclear and fossil-fuelled, water-cooled power plants. Experiments have so far been carried out to determine the general characteristics of crud behaviour in the CWL-3 loop and the effect on crud movement of variables such as boiling, heat flux and pH. This report describes the performance of the loop and preliminary experiments, the results of which delineate areas of crud behaviour requiring more systematic study.

2. THE CWL-3 LOOP

The loop is a closed circuit system constructed of 1.6 cm i.d. AISI type 316 stainless steel, designed to operate at 6.9 MPa and 288°C. A 7.5 kW canned-rotor centrifugal pump circulates water at 640 g s^{-1} through three preheaters in series, two test sections in parallel and a cooler. A general arrangement of the loop is shown in Figure 1 and details are given in Figure 2. The loop and counting system are described in detail by Rodd & Nicholson [1976].

The test sections are swaged Zircaloy-2 tubes, 0.95 cm i.d. x 0.16 cm wall thickness x 91 cm long. They are heated directly by a low-voltage a.c. power supply over a length of 64 cm. The top or downstream ends of the test sections are earthed and, at the inlet ends, insulating flanges electrically isolate the test sections and preheaters. In test section one, the maximum voltage is 33 V, giving a maximum power input of 100 kW at about 3000 A; a heat rating of 1500 W cm^{-1} and a heat flux of 500 W cm^{-2} are possible. Test section two is identical with test section one except that the power input is limited to 50 kW by the power supply system. Three stainless steel preheaters are similarly heated by an electric current but the heat fluxes are lower.

The chemical bypass loop can process cooled loop water at a rate of 300 g s^{-1}, or one loop volume a minute; the normal flowrate in the chemical loop is a quarter of this. The electrical conductivity of the water is monitored continuously and a Beckman meter indicates the oxygen concentration of a 6 g s^{-1} bypass flow as shown in Figure 2. Purification of loop water is effected by mixed-bed ion exchange followed by a Cuno 5 μm cellulose cartridge filter.

Deposition in the two test sections of crud with its radioactive iron-59 tracer is monitored by two heavily shielded gamma-scintillation counters. When rapid changes in deposition are anticipated, the counters are held stationary, monitoring 6 or 8 cm of the test sections, 50 cm downstream from the start of the heated section. When the system is steady, the counters scan the full length of the test sections. With millicurie quantities of iron of specific activity 10 mCi g^{-1}, crud deposits containing 10 mg m^{-2} of iron can be readily detected on the test sections; this is equivalent to a magnetite layer 2.6 nm thick.

3. EXPERIMENTAL

This section describes six experiments which can be divided into three phases:

- Injection of the crud into the loop and observation of its behaviour after injection and under the influence of changes in the loop operating conditions (*e.g.* power, flowrate, addition of alkali or acid).
- Examination of the deposit either *in situ* by autoradiography or gamma counting, or by X-ray analysis, electron microscopy, *etc.* following the removal and sectioning of the test sections.
- Removal of crud *in situ* by acids or complexing agents.

3.1 Methods

Radioactive iron-59 with a half-life of 45 days was produced by irradiating weighed specimens of pure iron (99.998 per cent) or mild steel shim for several weeks in a high-flux position in the AAEC reactor HIFAR. The 0.1 to 0.4 g specimens had a specific activity of about 100 mCi g^{-1} but were allowed to decay to 10 mCi g^{-1}, and sometimes further, before injection into the loop.

For Experiments 1 to 3, the specimens were dissolved in an excess of one molar nitric acid. Aliquots were diluted and injected directly into the loop *via* the makeup pump. Except where otherwise stated, AR grade chemicals were used. A delay of 2.5 minutes occurred before the first of the iron entered the chemical bypass line and a further few seconds were required before it entered the main loop. The injection and mixing were complete after a further 2.5 minutes.

In Experiments 4 and 6, iron was injected into the loop as solid magnetite prepared from an irradiated iron specimen dissolved in a 50 per cent excess of one molar sulphuric acid. Two moles of non-radioactive ferric iron as ferric alum in solution were added for each mole of radioactive iron. The mixture was poured into a large excess of boiling, four molar sodium hydroxide and the magnetite thus produced was washed by successive decantations. Three washes were possible before peptisation of the magnetite resulted in excessive losses of solid. The final rinse water had a pH less than 10.

The magnetite in suspension was placed in a vessel in a bypass in the chemical loop, pressurised with loop water and flushed through the chemical loop into the main loop. Mixing was complete within a minute.

The iron concentrations of isokinetic samples removed from the loop downstream of the main loop cooler were determined with a third scintillation counter. A comparison of the count rates of the sample and of a standard prepared from the original radioactive iron solution enabled iron concentrations to be measured down to 10 ng g^{-1}. No corrections for decay were required with this technique.

Before each experiment the loop water was purified and degassed to give a conductivity of less than 0.2 μS cm^{-1} and an oxygen concentration of about 70 ng g^{-1}. All pH values referred to in the text are for values measured at ambient temperature.

3.2 Experiment 1 - Deposition and Release at 25°C

3.2.1 Injection

The pH of the loop water was adjusted to 1.5 with nitric acid, and a solution of ferric nitrate containing 167 mg of iron labelled with iron-59 was injected into the loop. The iron was circulated in the loop for several hours while the three gamma-scintillation counters were calibrated against each other.

Raising the pH of the coolant to 11 with sodium hydroxide caused iron to deposit steadily on the loop surfaces over a period of 50 minutes, and the iron concentration in the circulating water to decrease from 16 to 1 µg g^{-1} (Figure 3). The deposits of 20 mg m^{-2} on test section 1A and 11 mg m^{-2} on test section 2A* were only about 0.36 per cent of the iron injected whereas the test sections provided 1.4 per cent of the total loop surface area; this implies substantial deposition on other surfaces, such as the preheaters. Turning the main circulator off and standing overnight had no effect on the deposits.

3.2.2 Removal of deposit

The loop was cleaned with triammonium citrate solution (41 mmol ℓ^{-1}) at pH 6.7. After 5.5 hours, 94 and 86 per cent of the iron previously deposited on test sections 1A and 2A respectively had been removed (see Figure 4).

3.3 Experiment 2 - The Effect of Heating

3.3.1 Deposition

The following conditions were established in the loop:

	Test Section 1A†	Test Section 2A
Test section inlet temperature (°C)	252	252
Test section outlet temperature (°C)	270	252
Power (kW)	39	0
Flowrate (g s^{-1})	264	264
Exit steam quality (%)	3.5	-
Exit subcooling (°C)	-	18
Heat rating (W cm^{-1})	610	0
Heat flux (W cm^{-2})	200	0

† Bulk boiling occurred in the downstream 25 cm of test section 1A.

Injection of a solution of radioactive iron (272 mg) in 1 molar nitric acid decreased the pH of the loop water from neutral to 3.0. The injected iron began to deposit on the boiling test section 1A about three minutes after the injection began and within a minute of first entering the loop (Figure 5). Very little iron deposited on the unheated test section 2A. The injection was complete after five minutes but deposition on test section 1A continued almost linearly until it

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*Other tubes subsequently used as test sections 1 and 2 are designated 1B and 2B *etc.*, respectively.

ceased after eleven minutes. During this initial period of fast deposition, the concentration of the circulating iron decreased from 29 to 20.5 $\mu g\ g^{-1}$ in fourteen minutes, so that while the 5.8 per cent of injected iron was depositing on the heated test section (0.7 per cent of total loop area) a total of 29 per cent deposited in the loop as a whole. A scan of the length of the test sections with the gamma-scintillation counters showed only a small variation in the thickness of the deposit over the length of the tubes, but a small maximum occurred on the heated test section 1A just downstream (at 50 cm) of the point of onset of bulk boiling at 39 cm (Figure 6). This maximum was measured as 766 $mg\ m^{-2}$ of iron, which is equivalent to a total thickness of 0.21 μm at the density of haematite [Perry *et al.* 1964].

Steady operation of the loop for three hours caused a small and similar increase in the deposits on both test sections, and a steady decrease in the amount of iron in the water from 20.5 $\mu g\ g^{-1}$ (71 per cent of the iron injected) to 5 $\mu g\ g^{-1}$ (17 per cent of that injected). That is, 54 per cent of the iron originally injected deposited during this three hour period. The small increases in the deposits on each of the test sections accounted for only 0.5 per cent of the injected iron so that deposition elsewhere accounted for most of the 54 per cent deposited. A survey of the loop after shutdown showed small concentrations of iron in the preheaters and in the main loop cooler.

After the three hours of steady operation, addition of sodium hydroxide to the loop raised the pH from 3.0 to 4.4 and gave rise to a small increase in the deposit on test section 1A but no increase in the deposit on test section 2A (Figure 5). The additional deposit on test section 1A was slowly and almost completely re-entrained during the following 30 minutes and the deposited iron returned to its former level. When more sodium hydroxide was added to raise the pH to 5.6 and then to 7.8, no increase was observed in the deposit on either test section, presumably because there was much less iron in the coolant; the concentration fell to less than 2 $\mu g\ g^{-1}$ after the first alkali addition.

3.3.2 Removal of deposit

Shutting down the loop had no effect on the deposits, and neither did startup and heating to 200°C after standing for several days.

When triammonium citrate (41 $mmol\ \ell^{-1}$) was circulated in the loop, the iron concentration in the circulating water rose quickly at first and then more slowly to give a maximum concentration of 13.6 µg g^{-1} after 45 minutes (Figure 7). The amount of iron in the water slowly decreased with continued operation of the loop. About 20 per cent of the deposit on the heated test section 1A and all the deposit on test section 2A were re-entrained.

Heating test section 2A with 30 kW, thus raising the surface temperature of the test section 40°C above that of the water, had no measurable effect either on the deposit on test section 2A or on the iron concentration in the water.

The iron in the water and on the test sections was not affected by an overnight shutdown followed by startup.

3.3.3 Examination of test sections

The test sections were removed from the loop for a closer examination of the deposits. An autoradiograph of test section 1A (Figure 8) shows that heavy deposits formed only on the heated part of the test section and virtually no deposit formed on the unheated section except for a small tail of deposit downstream. The autoradiograph shows a pronounced ripple in the amount of deposit along the length of the tube, but this was not apparent on visual inspection when the test section was sectioned along its length. However, the heavy deposition indicated by the peak in the autoradiograph at the upstream end of the test section adjacent to the copper electrical connection was clearly apparent to the eye and is shown in Figure 9. This heavy deposit corresponded exactly with a deep pit and heavy oxidation on the outside of the test section, apparently caused by overheating due to poor electrical contact between the Zircaloy test section and the copper electrical clamp. The deposit was heavy, uneven and rough, in marked contrast with the rest of the deposit on the heated test section which was mid-grey in colour with a light orange tint. The deposit on the unheated test section was slightly lighter grey with more orange. X-ray diffraction analysis of deposits from both areas revealed only haematite. Scanning electron micrographs of the general deposit on the heated area (Figure 10) show a maximum particle size of about 0.5 µm with many particles considerably smaller.

3.4 Experiment 3 - Boiling and Non-boiling at Constant Heat Flux

3.4.1 Deposition

Two new test sections, 1B and 2B, were installed in the loop. A power of 25 kW was applied to each test section and the coolant flowrates were adjusted to ensure bulk boiling in test section 1B and subcooling at the outlet of test section 2B, giving the following conditions:

	Test Section 1B	Test Section 2B
Inlet temperature (°C)	252	252
Outlet temperature (°C)	270	266
Power (kW)	25	25
Flowrate (g s^{-1})	177	354
Exit steam quality (%)	2.4	-
Exit subcooling (°C)	-	4.0
Heat rating (W cm^{-1})	390	390
Heat flux (W cm^{-2})	130	130

In contrast with Experiment 2, the injection of 244 mg of iron as ferric nitrate solution did not initially produce any large-scale deposition on either test section. After the injection, the pH was 2.6, as compared to 3.0 for Experiment 2. A number of small injections of sodium hydroxide totalling 11.2 millimoles increased the pH from 2.7 to 3.6 but, after operation for 100 minutes, only a very small amount of iron had deposited on the test sections (10 mg m^{-2} or 0.2 per cent of the 244 mg injected (Figure 11)). A 32 per cent reduction in the circulating crud during this period implied deposition elsewhere in the loop. The addition of a further 1.6 millimoles of sodium hydroxide raised the pH from 3.6 to 3.7 and initiated rapid deposition on both test sections, with significantly greater deposition on the boiling test section 1B. The amount of iron circulating decreased rapidly from 8 to 3.5 μg g^{-1}. The deposit on test section 1B rose to 320 mg m^{-2} after 30 minutes but there was insufficient iron present for a similar scale of deposition to have occurred throughout the loop.

At this point, the heaters and the main circulator tripped off and, within two minutes, 80 per cent of the deposited crud had left the heated surfaces of both test sections (Figure 11). The loop was restarted after two minutes with the full 25 kW applied to both test sections; the crud then redeposited even more rapidly than it had done before. Again, deposition was greater on the boiling test section 1B. After three minutes' operation, the power to both test sections was turned off but the preheaters and circulating pump were left on. Again, the crud left the test sections very quickly.

Thirty minutes later 2 millimoles of sodium hydroxide were added, raising the pH to 3.9, and 10 kW was applied to both test sections. Deposition recommenced on test section 1B but, except for a very small initial increase, not on test section 2B. Increasing the power to 20 kW increased the deposition rate on test section 1B but not on test section 2B. A later increase to 25 kW on both test sections had no effect on the rate of deposition on section 2B but increased the deposition on the boiling test section 1B. During this period, further additions of sodium hydroxide increased the pH to 4.4. The iron circulating in the loop during the steady increase in the test section 1B deposit gradually dropped to less than 10 ng g^{-1}.

Shutting down the loop again caused re-entrainment of the crud from test section 1B but, compared with the earlier shutdowns, the crud was held more tenaciously because the residual crud (90 mg m^{-2}) was greater and equilibrium took an hour to become established.

3.4.2 Removal of deposit

Restarting the main circulator the following day caused the iron concentration in the water to rise to 1.9 μg g^{-1} (Figure 12). Continued circulation of the water at ambient conditions had no effect on the deposit on the test sections.

To investigate the effect of adding alkali, 0.04 millimoles of sodium hydroxide were injected into the loop in small amounts, raising the pH from 4.5 to 6.7. Very little effect was noted on the test section deposits, but the iron in the loop water decreased slowly from 1.6 to 0.7 μg g^{-1} over several hours.

3.4.3 Examination of deposits

A gamma scan of the test sections after the run showed that the deposit upstream of both test sections was very small. The deposit on the non-boiling test section 2B was generally low but increased slightly towards the downstream end. The deposit on the boiling test section 1B increased linearly from the upstream end, levelled off after about one third of the length, dropped slightly and then peaked very sharply just before the downstream end (Figure 13). Although a small decrease in deposition occurred at the onset of bulk boiling, the change from subcooled to bulk boiling apparently had little effect. Deposition downstream of the heated part of test section 1B was greater than that in the centre of the heated section but this deposit decreased quickly as the distance from the heated region increased.

3.5 Experiment 4 - Magnetite

3.5.1 Deposition

A power of 39 kW was applied to cause boiling in test section 2B; test section 1B was unheated. This gave the following conditions:

	Test Section 1B	Test Section 2B
Inlet temperature (°C)	252	252
Outlet temperature (°C)	252	270
Power (kW)	0	39
Flowrate (g s^{-1})	264	264
Exit steam quality (%)	-	3.5
Exit subcooling (°C)	18	-
Heat rating (W cm^{-1})	0	610
Heat flux (W cm^{-2})	0	200

A suspension of magnetite containing 277 mg of iron was injected into the loop raising the pH to 7.8. The initial deposition was rapid on both test sections and, within 15 minutes, the deposits reached 30 mg m^{-2} and the magnetite circulating in the water decreased from 14.4 μg g^{-1} to 0.6 μg g^{-1} (Figure 14). On continued operation of the loop for 4.5 hours, the deposit on the boiling test section increased slowly to 78 mg m^{-2}, more than twice that on the unheated tube. Although the deposit generally increased on the boiling test section, some fluctuations occurred owing to removal and deposition of crud. The deposits on the test sections were not affected by shutting down the loop.

3.5.2 Examination of deposit

The travelling gamma-scintillation counters revealed that the deposits along both test sections were regular, the deposit on the heated test section 2B being about twice that on test section 1B (Figure 15). The unheated parts of test section 2B had the same amount of deposit as the unheated test section 1B. A tail of deposit downstream of the heated test section was not significant.

3.5.3 Stability of deposit

Starting the main circulator after standing overnight caused the iron concentration in the water to rise to a maximum of 1.7 μg g^{-1}

after two minutes, indicating that some iron had been removed from the surfaces. The iron concentration in the water fell slowly as the iron was redeposited (Figure 16). Neither stopping the circulator nor applying 40 kW to test section 2B had any effect on the deposits or on the amount of iron circulating.

3.6 Experiment 5 - The Effect of Acid and Alkali Additions on Deposited Magnetite

3.6.1 Injection of nitric acid

With the crud remaining on the test section from Experiment 4, the loop was started and the same conditions were established. The iron concentration in the water was 0.12 $\mu g\ g^{-1}$.

Injection of nitric acid decreased the pH from 7.8 to 4.2 and initiated a crud burst; the concentration of iron in the coolant rose abruptly to 2.1 $\mu g\ g^{-1}$. Deposition began immediately on the boiling test section 2B, whereas the unheated test section 1B showed no change. After 30 minutes, the iron circulating in the water had decreased to 0.84 $\mu g\ g^{-1}$ while deposition on the boiling test section 2B had slowed appreciably.

3.6.2 Injection of sodium hydroxide

Sodium hydroxide was injected into the loop to raise the pH from 4.5 to 8.8. The circulating iron dropped rapidly to 0.15 $\mu g\ g^{-1}$, but there was little initial change in the deposits on the test sections. Continued operation resulted in a decrease in the amount of iron deposited on the boiling test section 2B. Turning off the heaters caused a sharp increase in the deposit on test section 2B and a slow decrease in that on the non-boiling test section 1B (Figure 17).

Figure 18 shows the net change in the deposits along the two test sections during the experiment. The boiling test section 2B gained deposit along its heated length but the unheated test section 1B lost a small amount of deposit.

3.7 Experiment 6 - Different Boiling Rates at Constant Heat Flux

3.7.1 Deposition

With the same test sections as for Experiment 5, the following conditions were established in the loop without using the preheaters:

	Test Section 1B	Test Section 2B
Inlet temperature (°C)	252	252
Outlet temperature (°C)	270	270
Power (kW)	39	39
Flowrate (g s^{-1})	332	264
Steam quality (%)	1.5	3.5
Heat rating (W cm^{-1})	610	610
Heat flux (W cm^{-2})	200	200

The lower flowrate in test section 2B produced more vigorous boiling in that test section even though the heat fluxes were the same.

Injection of magnetite (276 mg of iron) into the loop, as in Experiment 4, resulted in greater deposition on the more vigorously boiling test section 2B (Figure 19). The deposition was very similar to that of Experiment 4 (Figure 14) with somewhat more deposition on both test sections; this was probably because the preheaters were switched off and thus not collecting as much crud as they did in the earlier experiment. Continued operation did not show the slow increase in deposition observed in Experiment 4 and, in fact, small decreases occurred in the deposits on both test sections. Except for the slightly larger deposits towards the inlet rather than the outlet ends, the pattern of deposition on the test sections during Experiment 6 was unexceptional (Figure 20).

3.7.2 Examination of deposits

The test sections were removed for a closer examination of the accumulated deposits from Experiments 3 to 6. A microdensitometer graph of test section 2B (Figure 21) generally confirms the gamma counting pattern of deposition shown in Figure 20. The differences can be attributed to the lack of fine collimation and statistical variations of the scintillation counters. The rippled pattern was not so evident as that observed in Experiment 2 (Figure 8).

Cutting the tube open revealed two slightly heavier spots of deposit which corresponded exactly with two overheating corrosion pits on the outside of the tube. The general deposit was very smooth and even, and thinner than the deposit of Experiment 2, appearing as little more than a dark brown discoloration on the surface of the Zircaloy. A slightly heavier deposit marked the position of the downstream edge of the downstream copper block; this is also apparent in Figure 21. Insufficient deposit could be removed by scraping to gain any information on the nature of the deposit by X-ray powder diffraction.

Electron micrographs of the accumulated deposits from Experiments 3 to 6 show that the crud consists of agglomerations of particles about 0.2 μm in diameter (Figures 22 and 23). The porous texture, apparent in Figure 23, is even more obvious under a stereo-viewer.

4. DISCUSSION

4.1 General Deposition

At pH values above 3 and at all temperatures, a decrease in the circulating crud was always observed after an iron injection or a crud burst. The time required for the bulk of the crud to deposit in each experiment was usually a matter of minutes, but this could be extended to an hour under acid conditions. At ambient temperature, deposition occurred uniformly on all loop surfaces although some accumulation in crevices, quiescent areas or in regions of high shear forces cannot be precluded.

4.2 Heating

Heating in the test sections of the CWL-3 loop implies some or all of the following conditions:

(a) A test section surface which is hotter than the adjacent fluid.
(b) Transfer of heat from the test section to the fluid.
(c) A temperature gradient in the fluid.
(d) Bubble formation on the surface and on deposited crud.
(e) Bubble growth and/or collapse at the surface and/or in the fluid.
(f) An increase in the fluid temperature along the test section up to, and perhaps beyond, the saturation temperature.
(g) A change in the hydrodynamic behaviour of the fluid up the test section as a result of subcooled and/or bulk boiling.

Whilst heating clearly promotes deposition in the test sections, it is not possible in the present experiments to distinguish the relative importance of these individual effects. In particular, the extent to which the enhanced deposition can be ascribed to the presence of boiling is open to question.

Experiments with one test section heated and the other unheated resulted in large deposits on the former but very little on the latter.

When both test sections had the same heat flux, greater deposition occurred in the test section with the lower coolant flowrate. Preferential deposition on heated surfaces occurred not only during periods of crud injection but also after a crud burst had occurred. Crud was removed from unheated surfaces within several minutes and redeposited within 20 minutes on a heated surface.

These observations agree qualitatively with the findings of Picone & Fletcher [1966], and also those of Charlesworth [1970] and Mankina [1960] who suggested that deposition was proportional to the square of heat flux.

Deposition on the heated surfaces of the test sections usually took the form of an initial period of fast growth when the bulk of crud deposited, followed by a period of very much slower growth. The initial period which normally lasted about ten minutes, depending on the particular conditions, coincided with the presence of a significant amount of iron in the circulating water, but no quantitative relationship between deposition rate and crud concentration was observed. The period of slow growth was confined to heated surfaces and, under constant conditions, existed for the remainder of the experiment when iron was present in the water in only very small amounts, usually less than 100 ng g^{-1}. Although representing only a very small rate of deposition, slow growth may be significant in a large power-producing circuit where weeks and months are available for the accumulation of crud. Charlesworth [1970] noted that under constant conditions, crud deposits reached an equilibrium level, but in the present experiments there was no evidence of this occurring on the heated surfaces of the CWL-3 loop, although it may occur in long-term experiments. It is interesting to note that even though Charlesworth reported equilibrium deposits, he had to inject crud constantly to maintain the crud concentration in the coolant.

Bulk boiling - the onset of which can be calculated accurately - occupied less than half the length of the heated test sections, and in the upstream portion of the test sections only subcooled boiling occurred. A uniform heat flux existed along the length of the test sections and, in general, deposition commenced with heating and continued uniformly along the tubes without showing discontinuities which could be correlated with the onset of bulk boiling. Thus, it is concluded that bulk boiling is not a prime prerequisite for preferential deposition on a heated surface.

The situation for subcooled boiling is different. Our observations are compatible with subcooled boiling being a major factor in crud deposition processes. The correlation of Thom *et al.* [1965-66] relating the onset of subcooled boiling to heat flux, flowrate and subcooling, shows that under the normal operating conditions of the loop extensive subcooled boiling commenced at the inlet to the heated test sections. In fact, with an inlet temperature of 252°C and a flowrate of 264 $g\ s^{-1}$, the power normally supplied to the heated test sections (39 kW) was 240 per cent of that required to cause subcooled boiling at the inlet.

In Experiment 3, with one boiling and one non-boiling test section, there was extensive deposition in the boiling test section but comparatively little in the non-boiling test section. Under the conditions of this experiment, the boiling test section was supplied with 25 kW of power, 210 per cent of that required to cause subcooled boiling at the inlet. The non-boiling test section was supplied with 25 kW, 113 per cent of the power required to cause subcooled boiling. Thus, where there was very little subcooled boiling there was very little deposition.

Although it is possible that other effects are active, the experiments are consistent with subcooled boiling being an important cause of crud deposition. This agrees with the observation of Charlesworth [1970] that with subcooling sufficient to prevent subcooled boiling in a pressurised water system, the amount of deposit formed was very much less than in the subcooled boiling region of boiling systems. Picone & Fletcher [1966] observed, during experiments in the Saxton reactor, that deposition of crud began approximately where subcooled boiling began. On the other hand Katz [1957], who observed a strong correlation between crud deposition and heat transfer (or neutron flux), reported that there was no difference, except in appearance, between deposits formed in the presence and absence of subcooled boiling.

The enhancement of crud deposition on heated surfaces and the rapidity with which it occurred were no doubt contributing factors in the damaging deposits observed on fuel in boiling water reactors such as the Winfrith Steam Generating Heavy Water Reactor (SGHWR), Big Rock Point and Humboldt Bay [Cartwright *et al.* 1969, Cohen 1969].

4.3 Influence of Loop Chemistry

Except for the additions of crud, acid and alkali, the chemistry of the loop was maintained constant with an oxygen concentration of 70 $ng\ g^{-1}$ and impurities giving a conductivity less than 0.2 $\mu S\ cm^{-1}$.

The experiments show that additions of acid or alkali have a marked effect on the rate of both deposition and re-entrainment of crud. In general, an addition of alkali favours deposition, while acid favours re-entrainment. An addition of 2 millimoles of nitric acid in Experiment 5, which changed the pH measured at room temperature from 7.5 to 4.0, caused a rapid re-entrainment of crud, particularly from the isothermal surface of the loop, to give a significant crud burst; addition of alkali then accelerated the redeposition of the crud.

Crud did not deposit readily from solutions of low pH even when significant quantities of crud were present in suspension.

In Experiment 3 with a coolant pH of 3.6, deposition was very slow but it was sharply increased by the addition of only 1.6 millimoles of sodium hydroxide. The effect of low pH could be overcome to some extent by increasing the power input as was shown in Experiment 2 where, with a pH of 3 and a heat rating 56 per cent greater than that used in Experiment 3, very large quantities of crud deposited. It is, however, noteworthy that at pH 3 the transition from fast to slow deposition rates occurred when the crud concentration in the coolant was still high.

The present results relating a decreased crud mobility to increased pH agree with Robertson [1961] and Simon [1958] who reported that an increase in pH, although it does not reduce the specific deposition rate, decreases the release rate and hence the crud concentration in the coolant, resulting in a net reduction in crud deposited. Robertson [1961] and Picone [1963], however, in contradiction with the above reports, observed that crud deposits laid down at neutral pH were removed by the addition of alkali, but this may have been caused by a crud burst followed by redeposition elsewhere. It is now general practice to add lithium hydroxide or ammonia to the cooling circuits of closed-cycle reactors [Cohen 1969] to decrease crud accumulation on heated surfaces by reducing both the formation of crud by corrosion processes and its transport around the cooling circuits.

4.4 Haematite and Magnetite

The experiments showed some notable differences in the behaviour of the haematite and magnetite forms of crud but this may have been caused, at least in part, by their different methods of production. In the formation of haematite *in situ* by the addition of alkali, goethite probably existed as an intermediate for some time at 25°C and for up to several hours at 240-270°C [Butler & Ison 1965, Gainsford *et al.* 1973].

Magnetite, on the other hand, was precipitated with concentrated sodium hydroxide and washed before injection into the loop. Scanning electron micrographs show the deposited particles from the different experiments to be similar in size and less than 0.5 μm. The particles identified as haematite from ferric nitrate injections appeared to be more crystalline. Haematite remained in suspension longer than magnetite and magnetite crud was generally less mobile than haematite. The greater mobility of haematite was probably the cause of its greater concentration on heated surfaces.

4.5 Pattern of Deposition

As we have seen, the patterns of deposit obtained on the test sections were broadly in accord with the uniform heating distribution. However, there were irregularities in the fine structures of the deposits. For instance, peaks of deposition were observed adjacent to the upstream and downstream connections which, in some cases at least, were caused by overheating. Also, prominent and regular ripples were evident in some deposits; possible explanations for this include electrical or magnetic effects produced by the alternating electric current, mechanical vibrations of the tubing, or a hydrodynamic effect.

Differences were also observed in the deposition behaviour of magnetite and haematite cruds which can be attributed to the more rapid deposition of magnetite. Haematite deposition generally increased along the heated section towards the downstream end whereas deposits after magnetite injection were more evenly distributed along the length of the tube. Also, haematite deposition continued for a few centimetres beyond the downstream end of the heated section. This concentration of haematite deposit at the downstream end of the heater and beyond, can be attributed to a release and redeposition mechanism which swept the more mobile haematite towards the hotter regions.

4.6 Stability of Deposit

The ease with which deposits were re-entrained varied widely. Some deposits were very stable, not being affected by a change in pH or by shutdown but some deposits, notably those of Figures 7 and 11, were re-entrained by the removal of power to the test sections or by the addition of acid.

In general, deposits formed on unheated surfaces were more readily removed although the deposits induced by adding alkali, illustrated in Figure 11, were a notable exception. The stability of the deposit on heated surfaces is also evidenced by their greater resistance to removal by chemical cleaning agents. In Experiment 2, all of the iron deposited on the unheated test section was re-entrained with the aid of triammonium citrate while only 20 per cent of the iron on the heated test section was removed.

4.7 Electrical and Magnetic Effects

No attempt has yet been made in these experiments to test directly whether magnetic or electric factors have an influence on crud deposition. Experiment 3, in which the test sections had the same power but different coolant flowrates, showed that if any such influence existed then it was much smaller in magnitude than the influences of heating.

5. CONCLUSIONS

The loop and the radioactive method of following crud deposition provide a useful technique for studying crud deposition on heated surfaces. Crud deposits of the order of 4 mg m^{-2} were measured using millicurie quantities of iron of specific activity 10 mCi g^{-1}.

The preliminary experiments described in this report showed that:

- Under steady operating conditions at pH values greater than 3, crud always tended to deposit. Deposition was favoured by the addition of alkali. The bulk of any circulating crud deposited rapidly within minutes or hours of injection, and this rapid deposition was usually followed by a very much slower mass transfer onto heated surfaces from elsewhere in the loop, even when low concentrations of iron were present in the water.
- Deposition of crud occurred preferentially on heated surfaces - especially on hot spots - but not to the exclusion of deposition on unheated surfaces. Magnetite crud deposited more rapidly than haematite, was less mobile and was more evenly distributed between heated and unheated surfaces.
- Subcooled boiling was apparently a more important factor than bulk boiling in the enhancement of crud deposition.
- Unsteady conditions such as a lowering of pH or removal of power caused crud bursts, but only a fraction of the deposited crud was involved.

Future experiments are planned to investigate more closely certain of the phenomena observed in these initial experiments. They include the greater stability of heated and aged crud, and the role of subcooled boiling. Attention will also be given to in-service cleaning methods such as removal of crud by injections of nickel.

6. ACKNOWLEDGEMENTS

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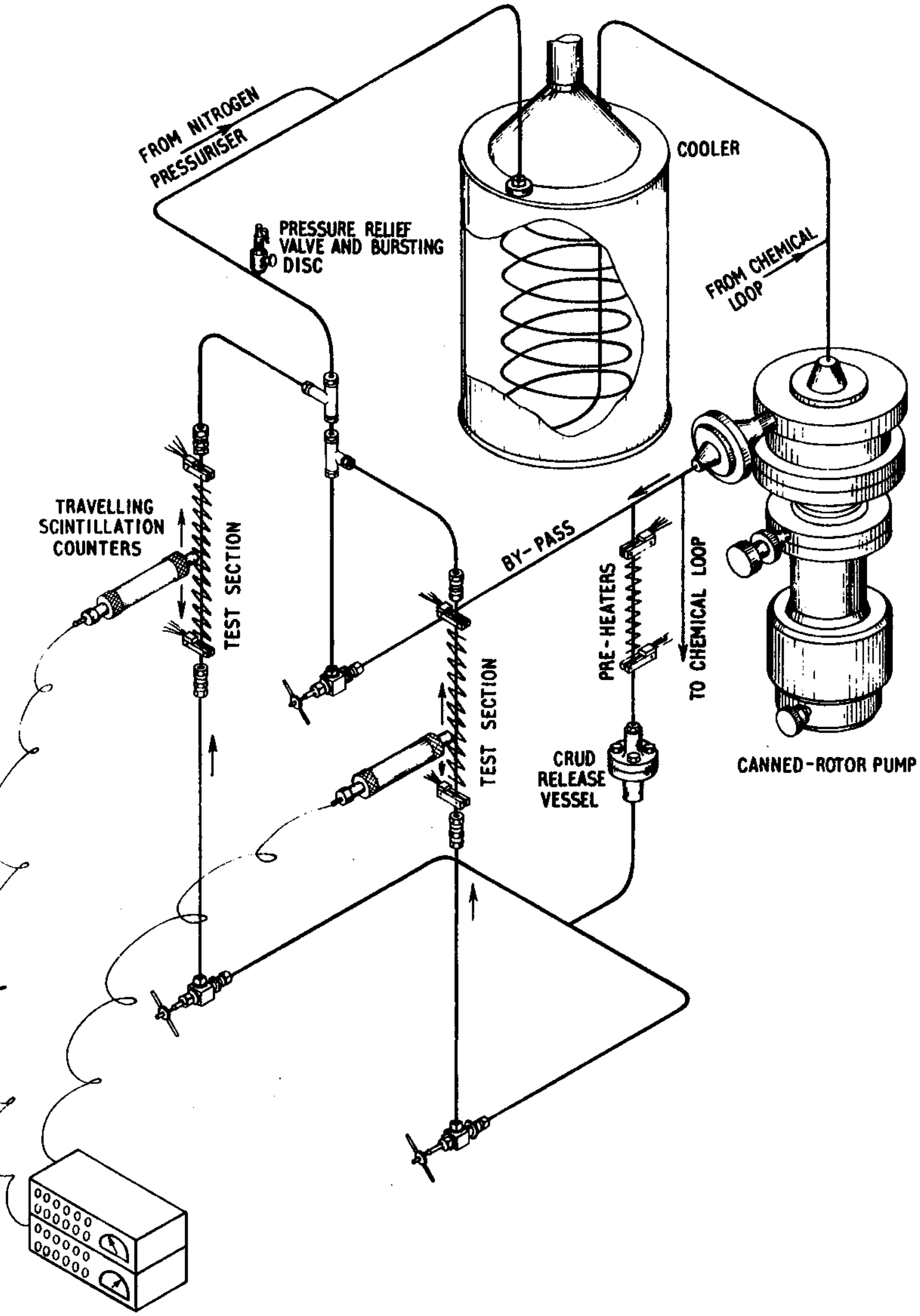


FIGURE 1. CWL-3 MASS TRANSFER LOOP

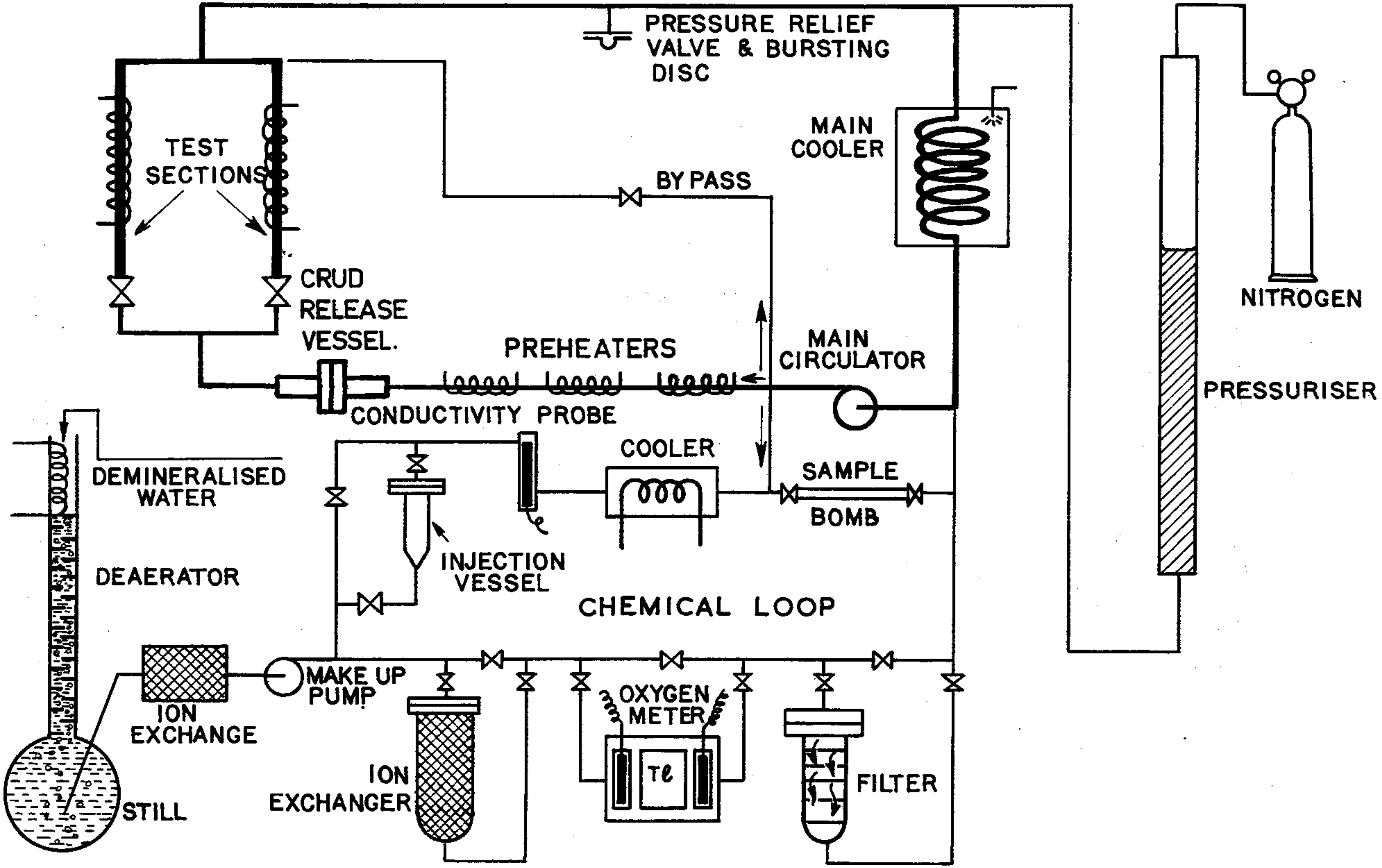


FIGURE 2. EQUIPMENT FLOWSHEET FOR THE CWL-3 MASS TRANSFER LOOP

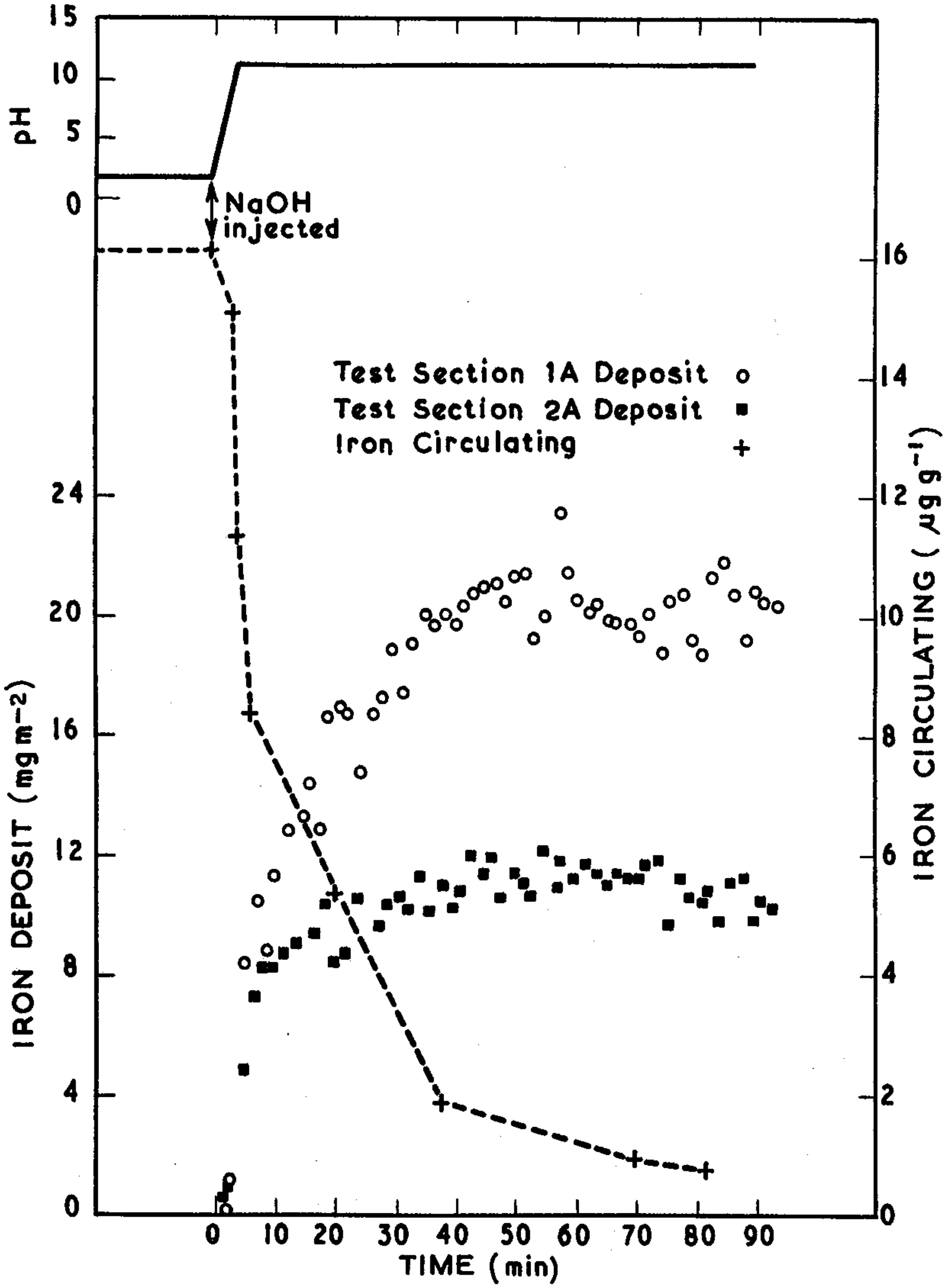


FIGURE 3. REMOVAL OF IRON FROM SOLUTION AND DEPOSITION ON THE TEST SECTIONS AT AMBIENT TEMPERATURE. EXPERIMENT 1.

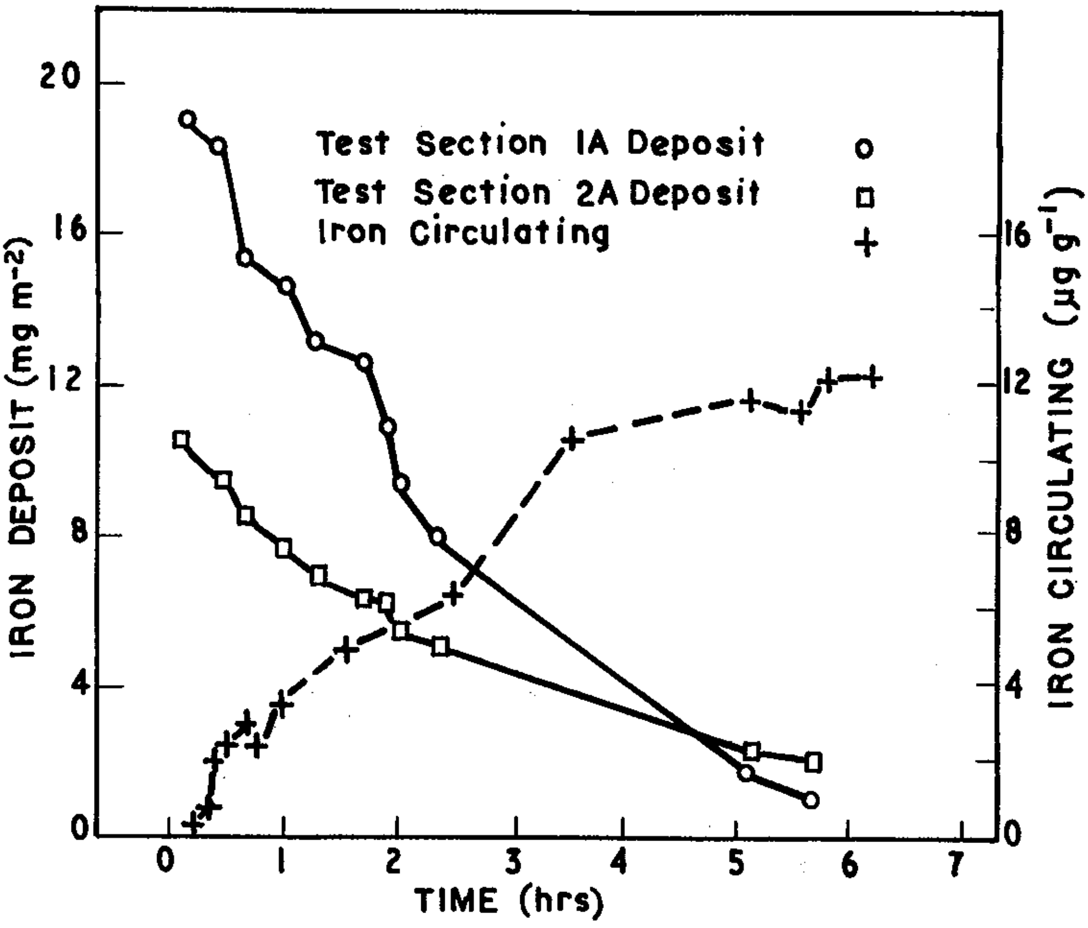


FIGURE 4. REMOVAL OF DEPOSIT DURING EXPERIMENT 1 FOLLOWING THE ADDITION OF TRI-AMMONIUM CITRATE

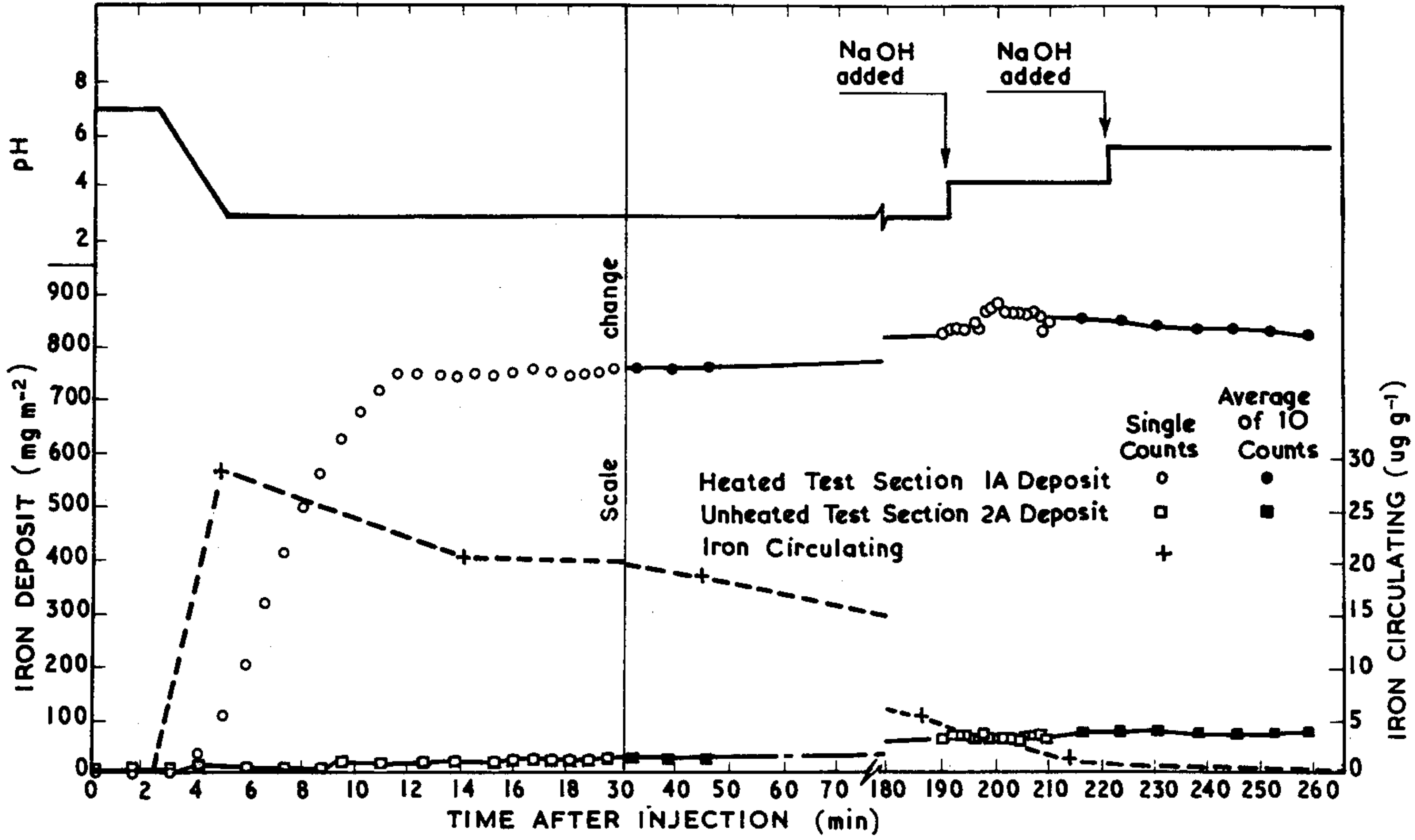


FIGURE 5. DEPOSITION OF IRON DURING EXPERIMENT 2.

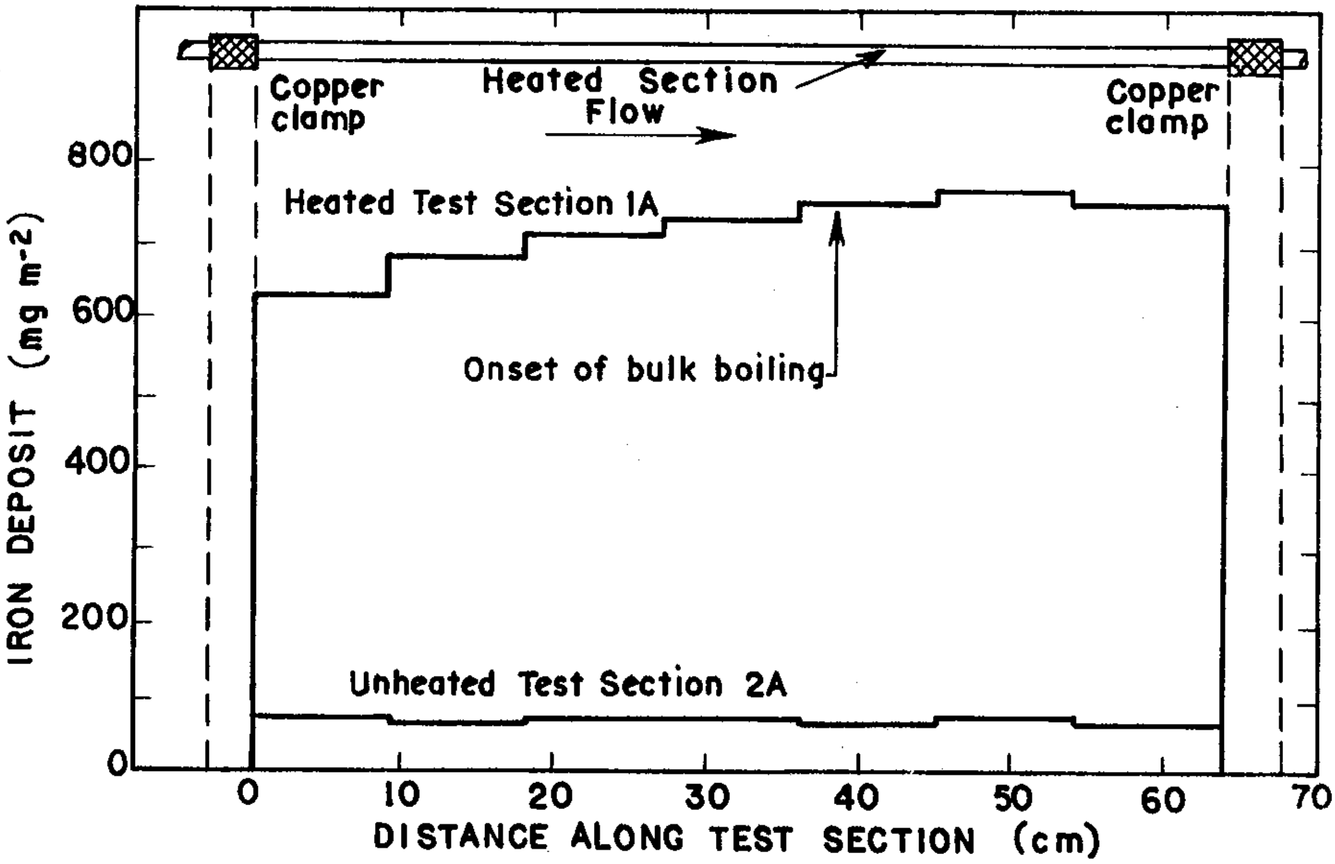


FIGURE 6. VARIATION OF DEPOSITION ALONG TEST SECTIONS. EXPERIMENT 2

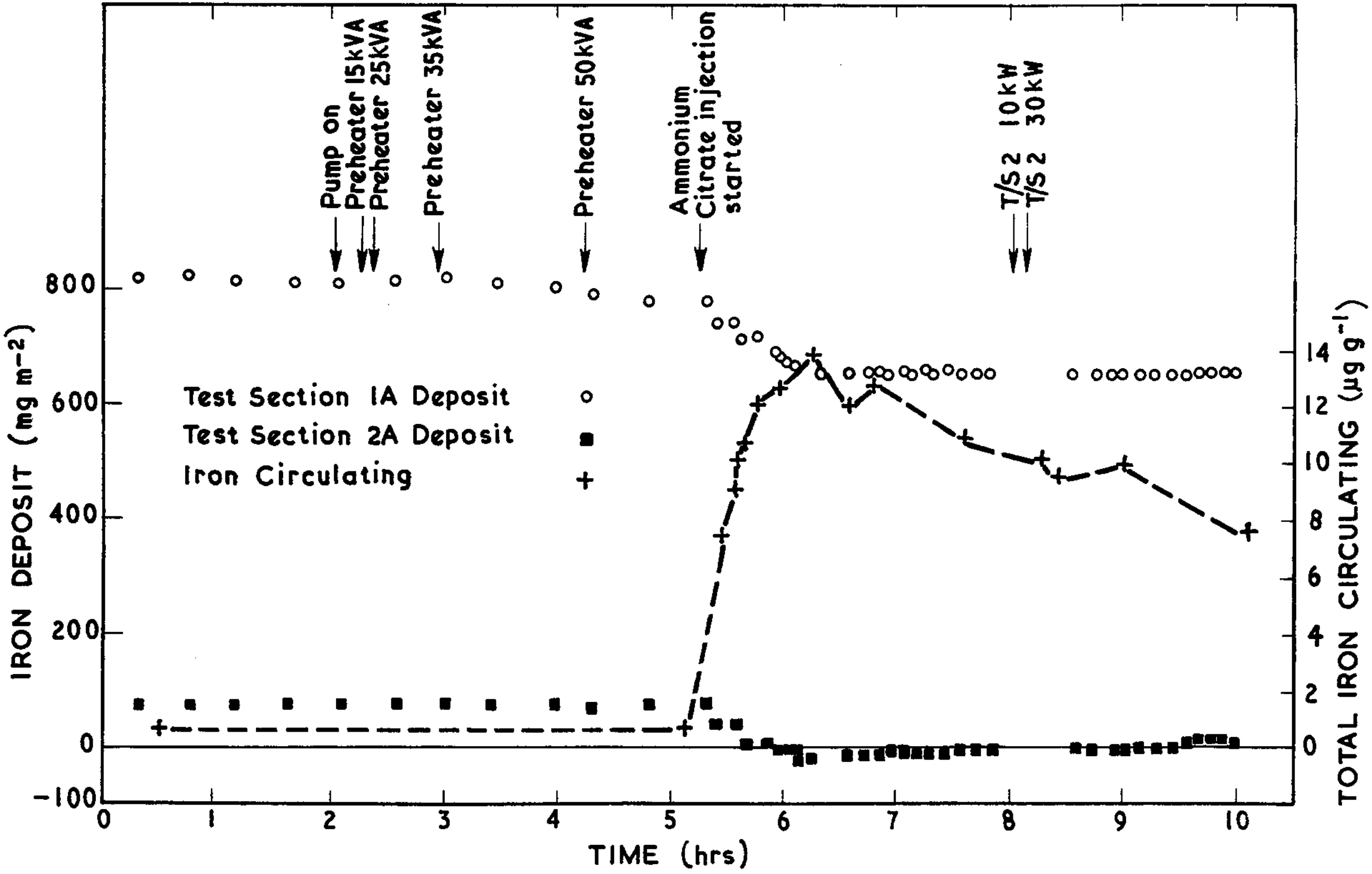


FIGURE 7. RE-ENTRAINMENT OF CRUD DURING EXPERIMENT 2.

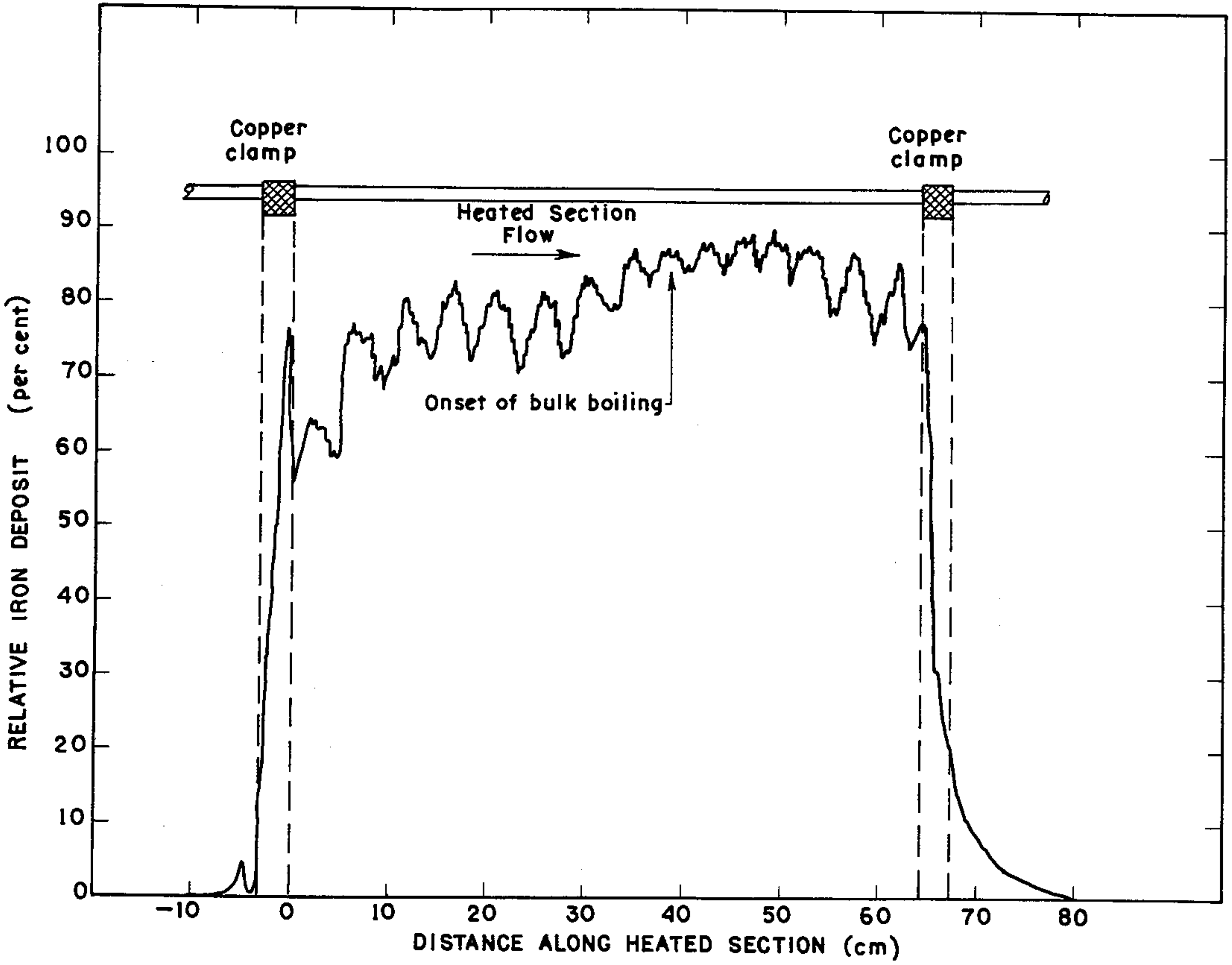


FIGURE 8. IRON DEPOSITED ON THE BOILING TEST SECTION DURING EXPERIMENT 2

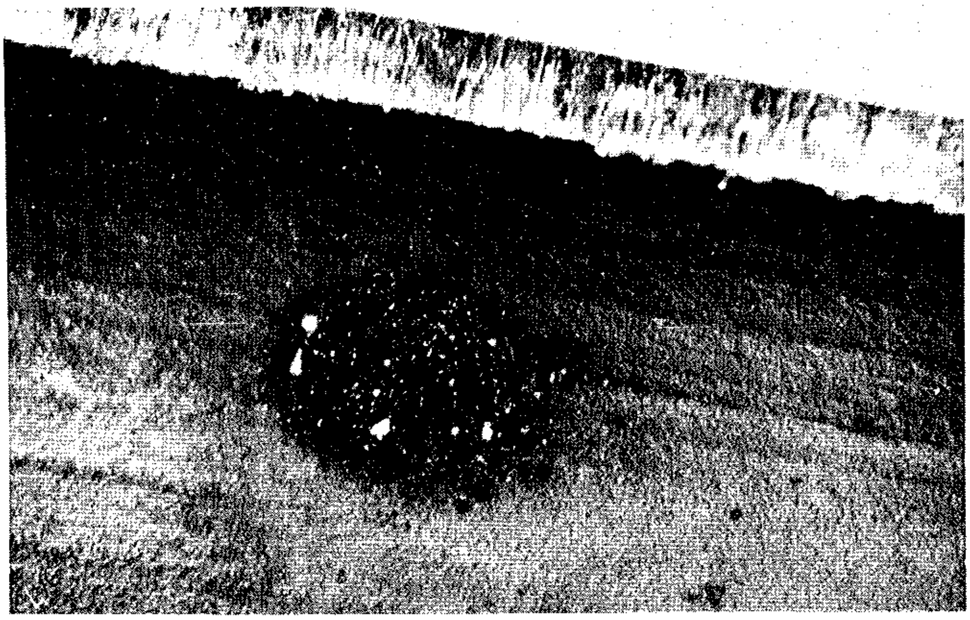
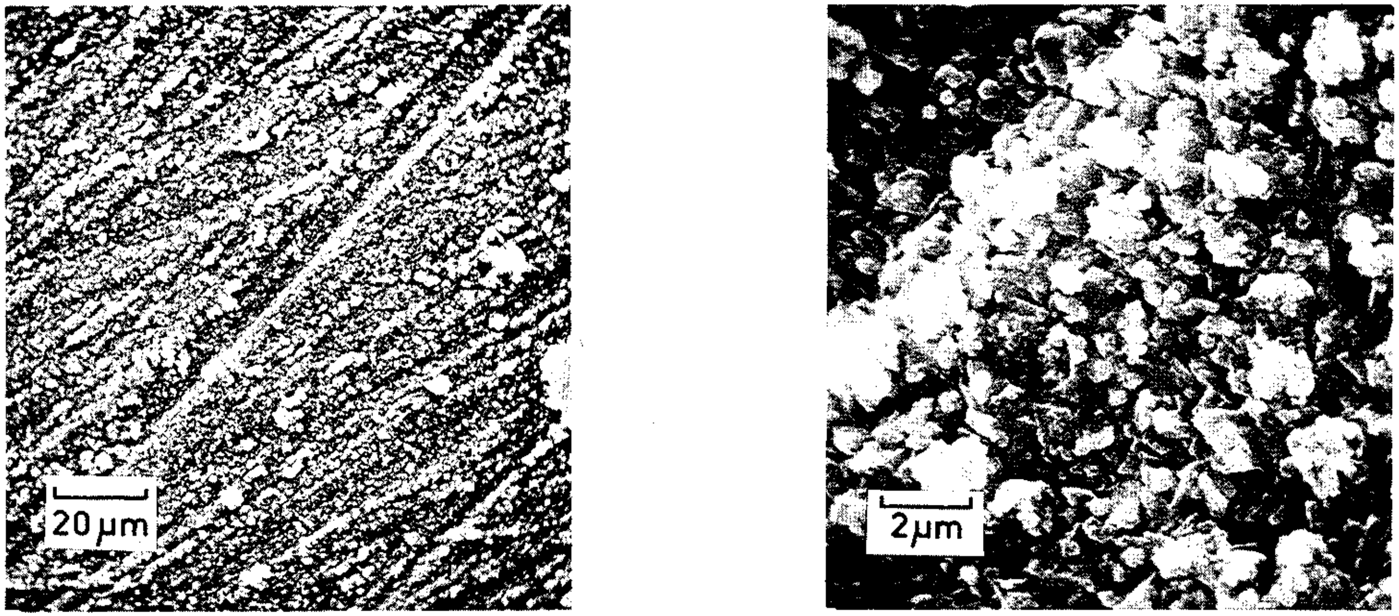


FIGURE 9. HEAVY DEPOSIT AT THE UPSTREAM END OF TEST SECTION 1A



(a) ×600

(b) × 6000

FIGURE 10. SCANNING ELECTRON MICROGRAPHS OF THE GENERAL DEPOSIT ON TEST SECTION 1A AFTER EXPERIMENT 2

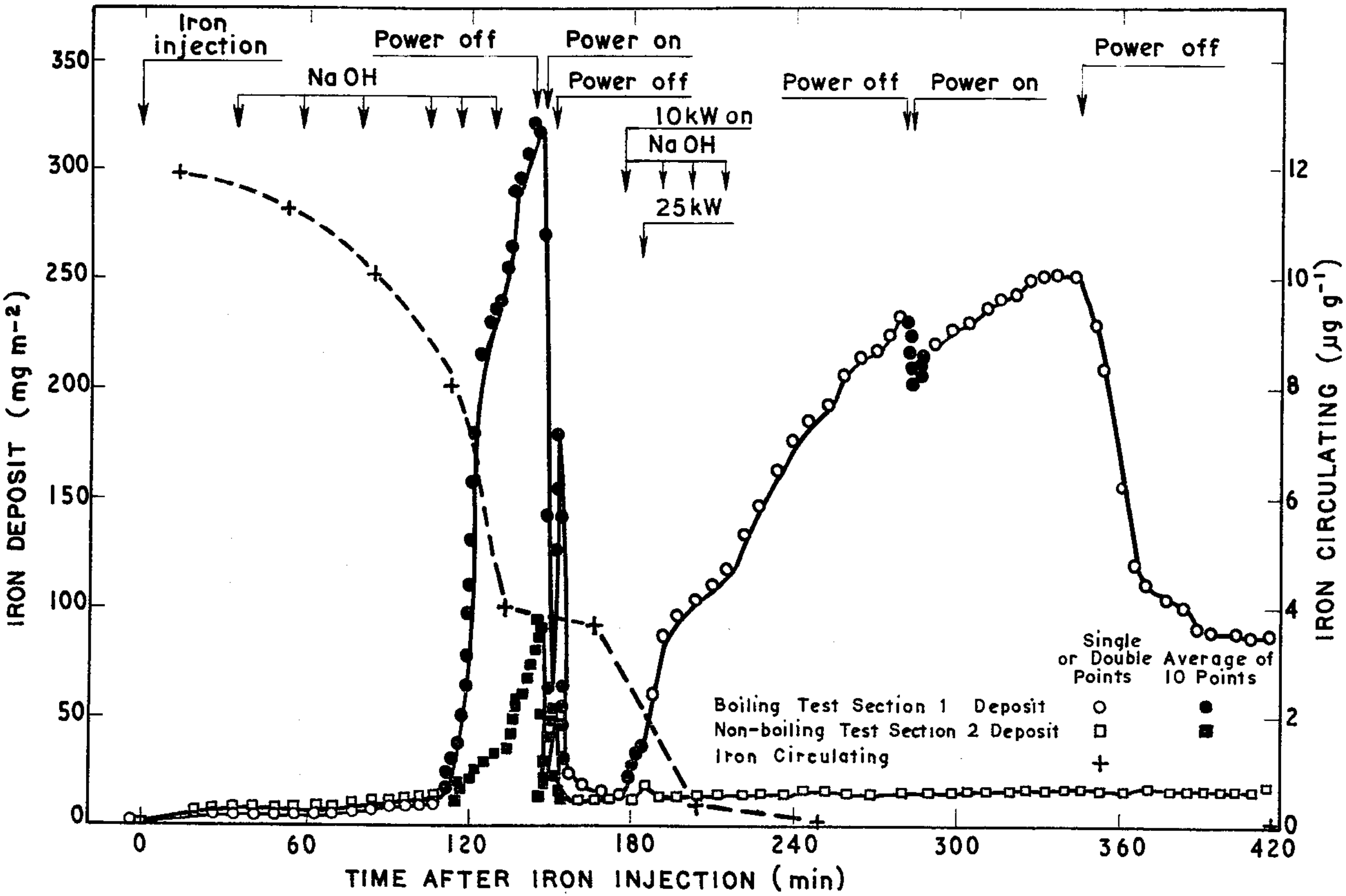


FIGURE 11. DEPOSITION ON BOILING AND NON-BOILING SURFACES. EXPERIMENT 3

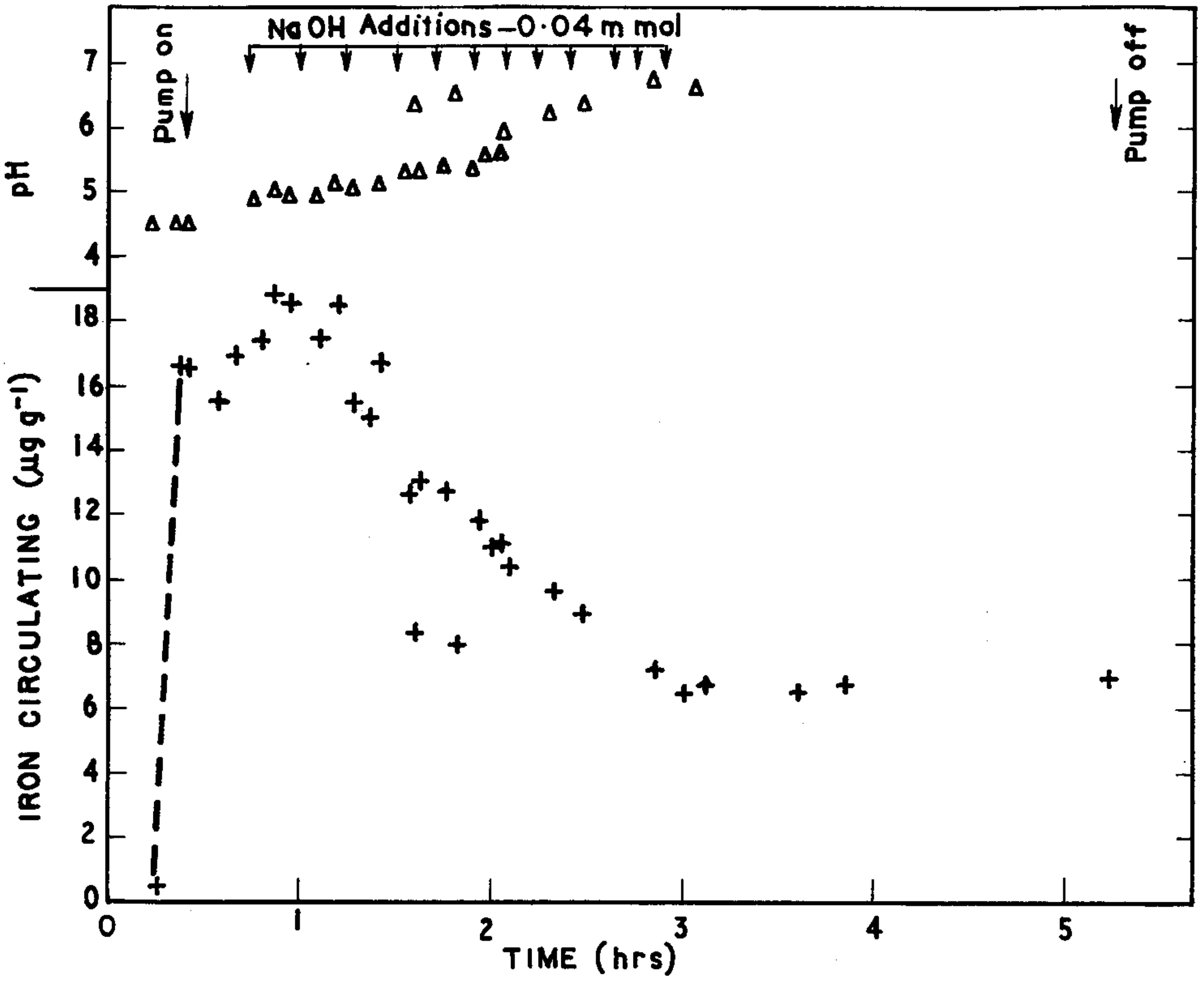


FIGURE 12. RE-ENTRAINMENT OF IRON DURING EXPERIMENT 3 WITH NO HEATERS ON

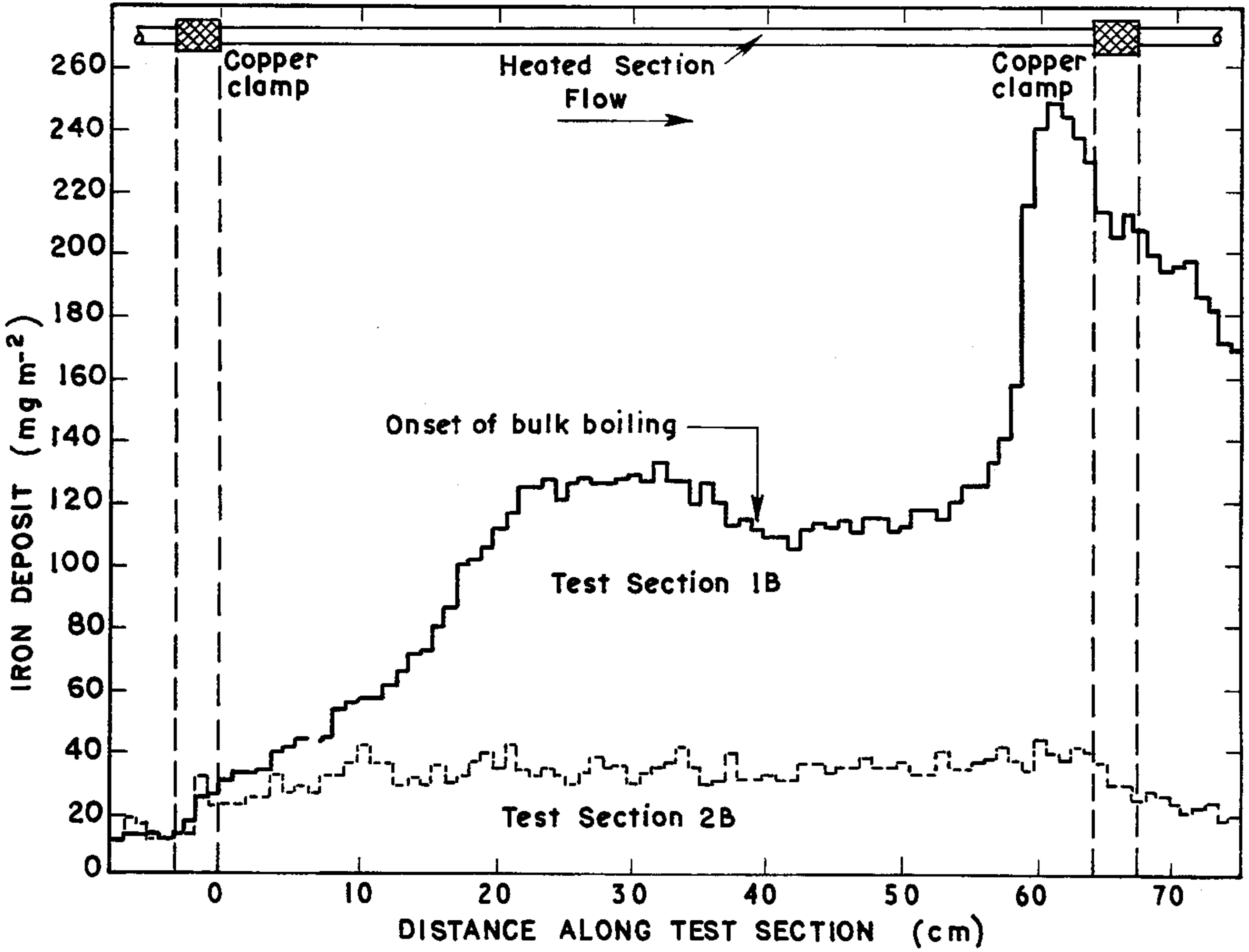


FIGURE 13. VARIATION OF DEPOSIT ALONG THE TEST SECTIONS AFTER EXPERIMENT 3

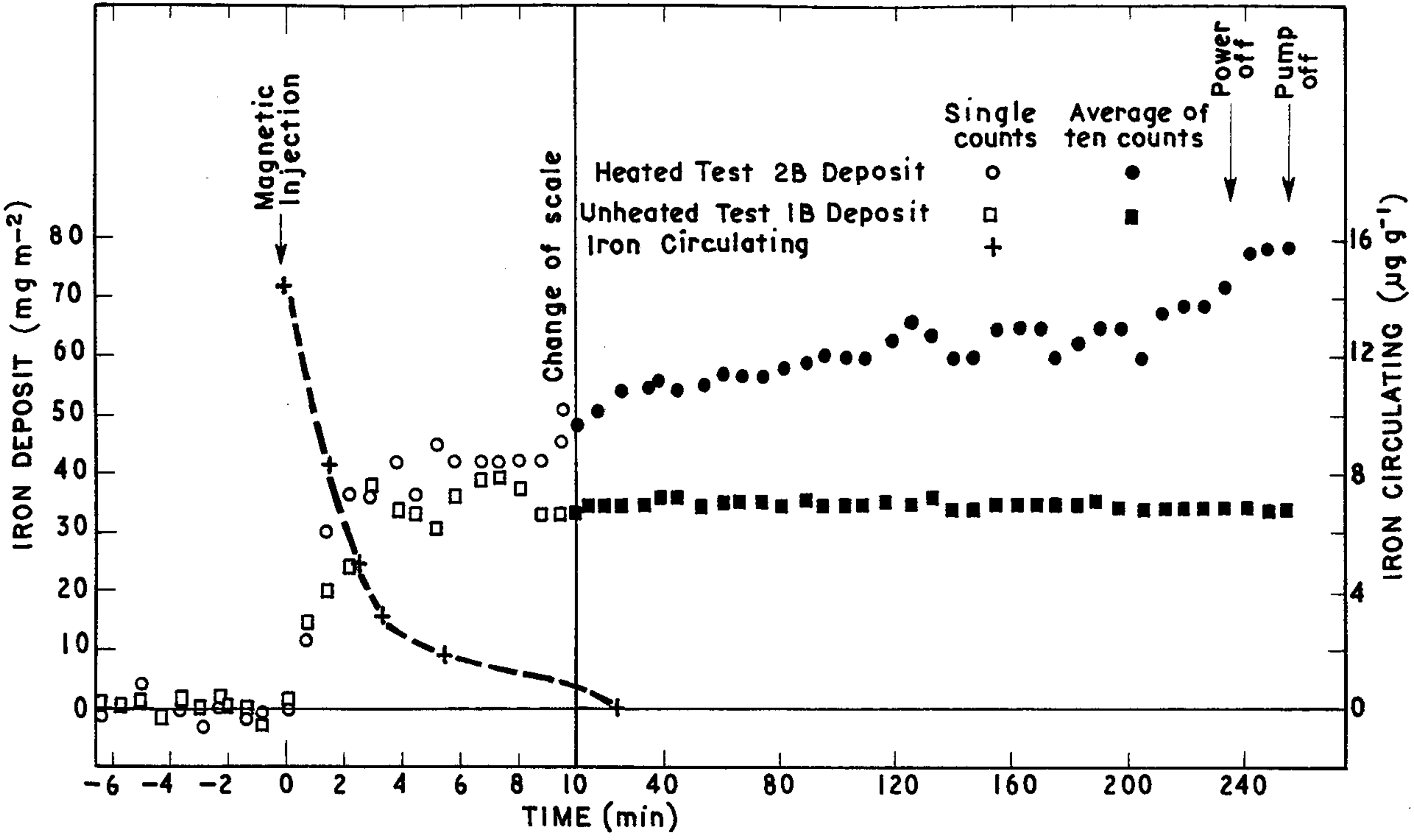


FIGURE 14. MAGNETITE DEPOSITION ON HEATED AND UNHEATED TEST SECTIONS. EXPERIMENT 4

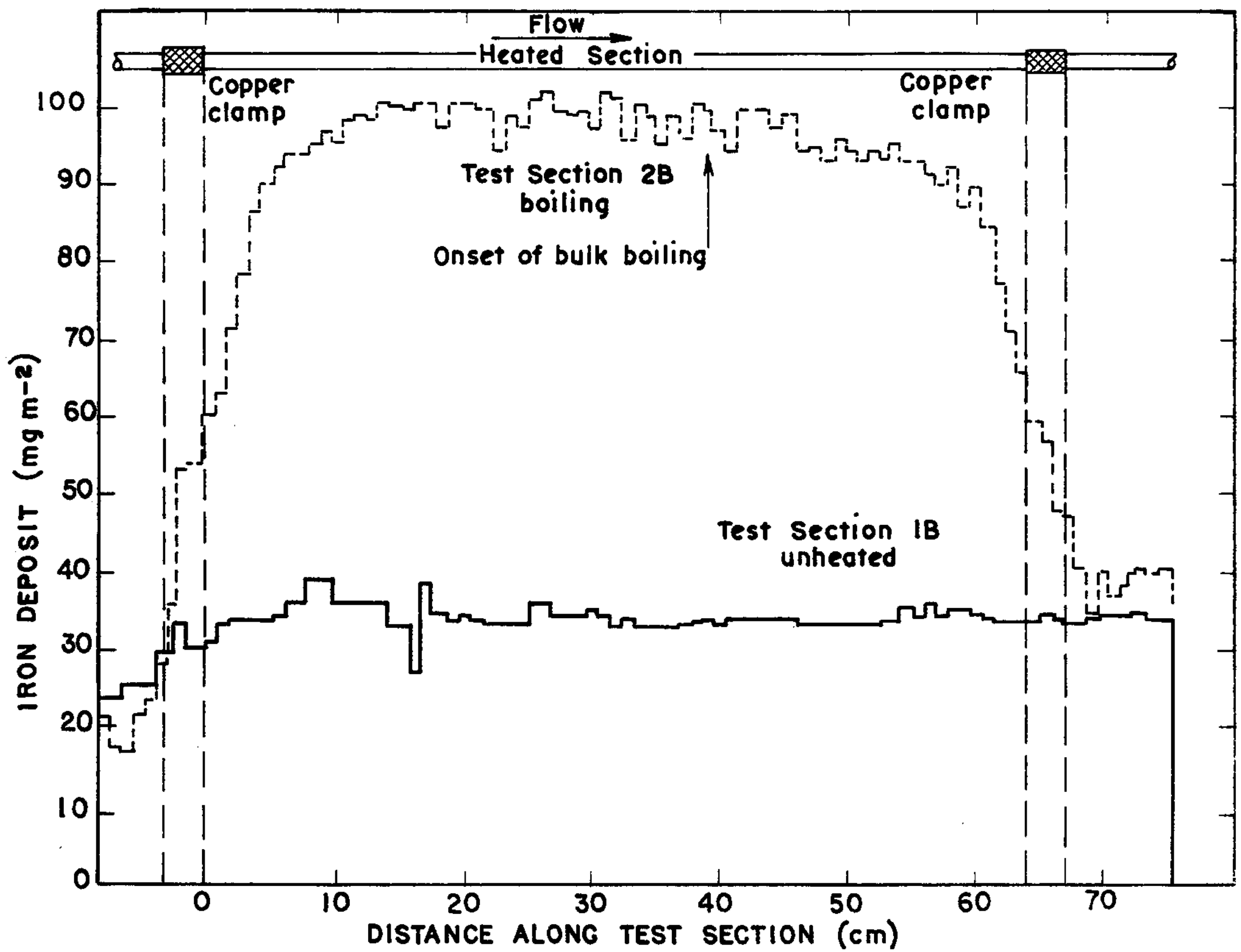


FIGURE 15. VARIATION OF DEPOSIT ALONG THE TEST SECTIONS AFTER EXPERIMENT 4

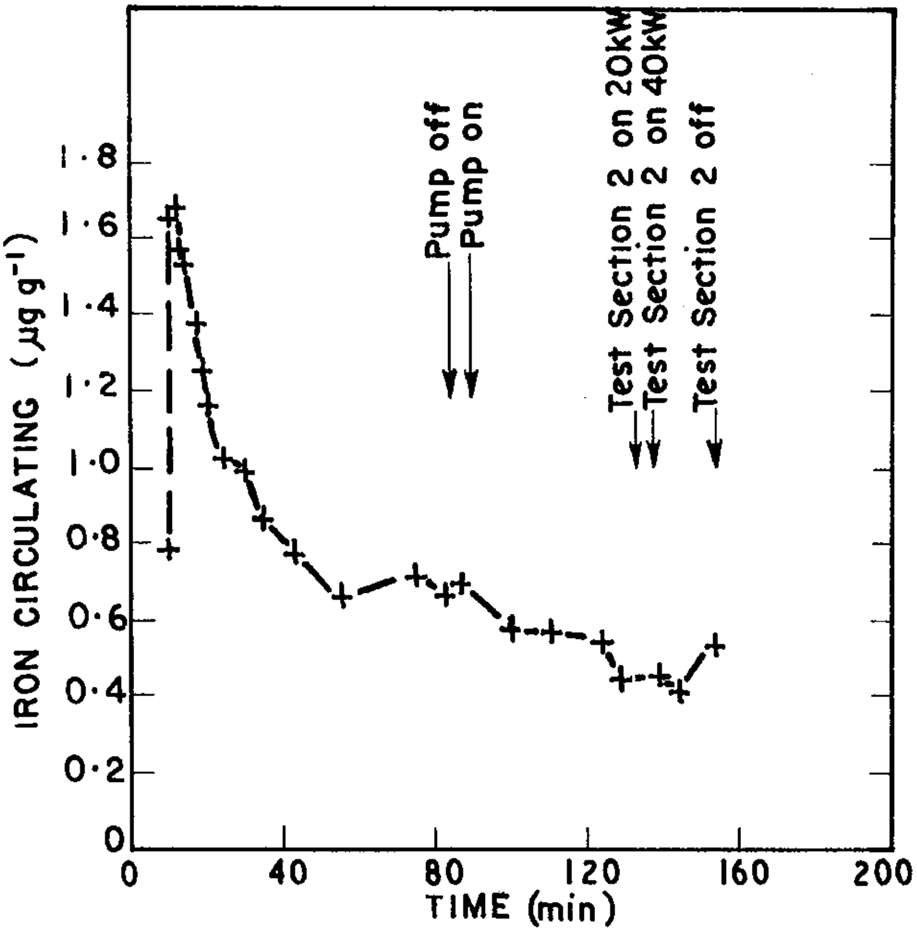


FIGURE 16. RE-ENTRAINMENT OF IRON DURING EXPERIMENT 4

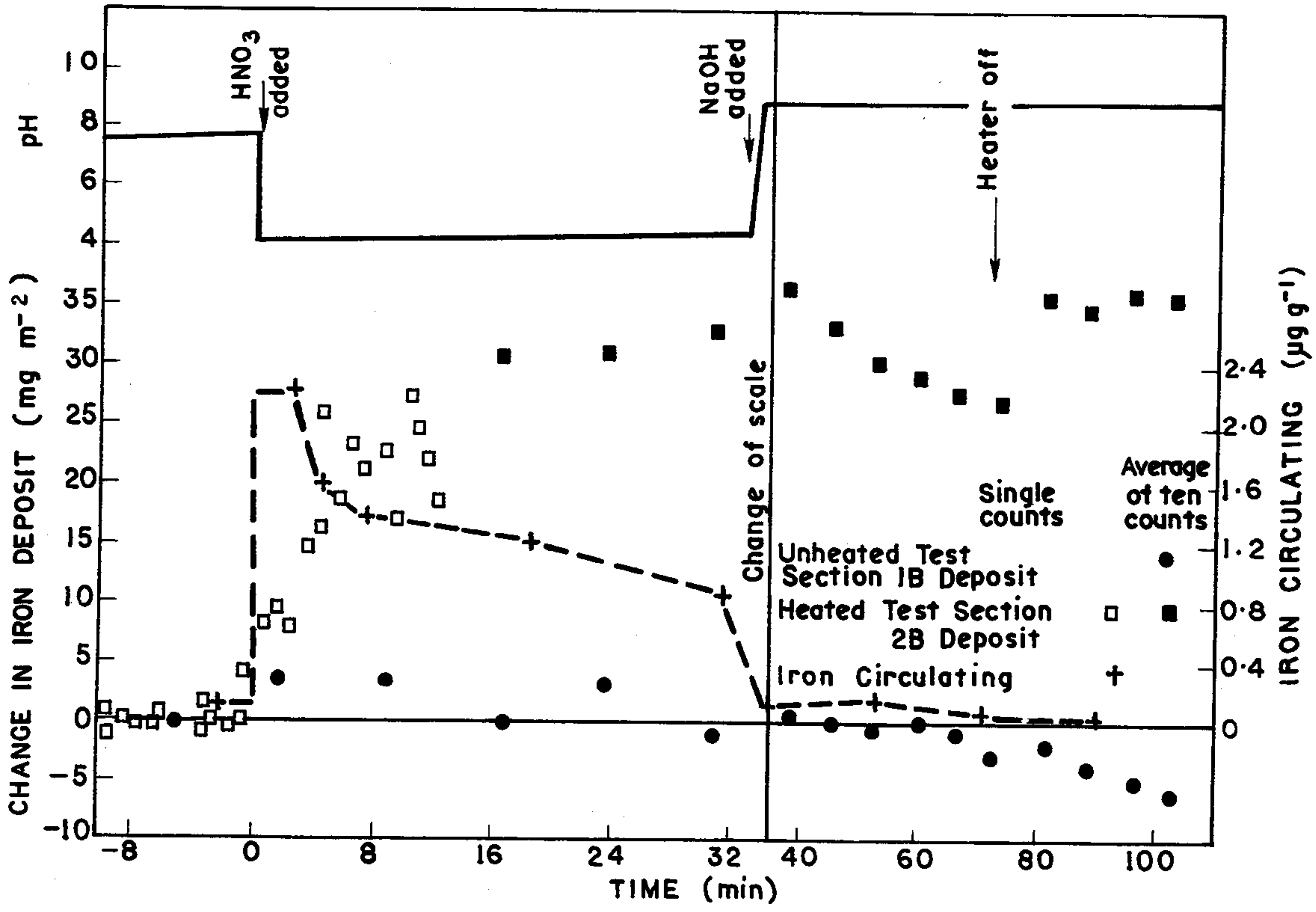


FIGURE 17. A CRUD BURST CREATED BY THE ADDITION OF NITRIC ACID. EXPERIMENT 5

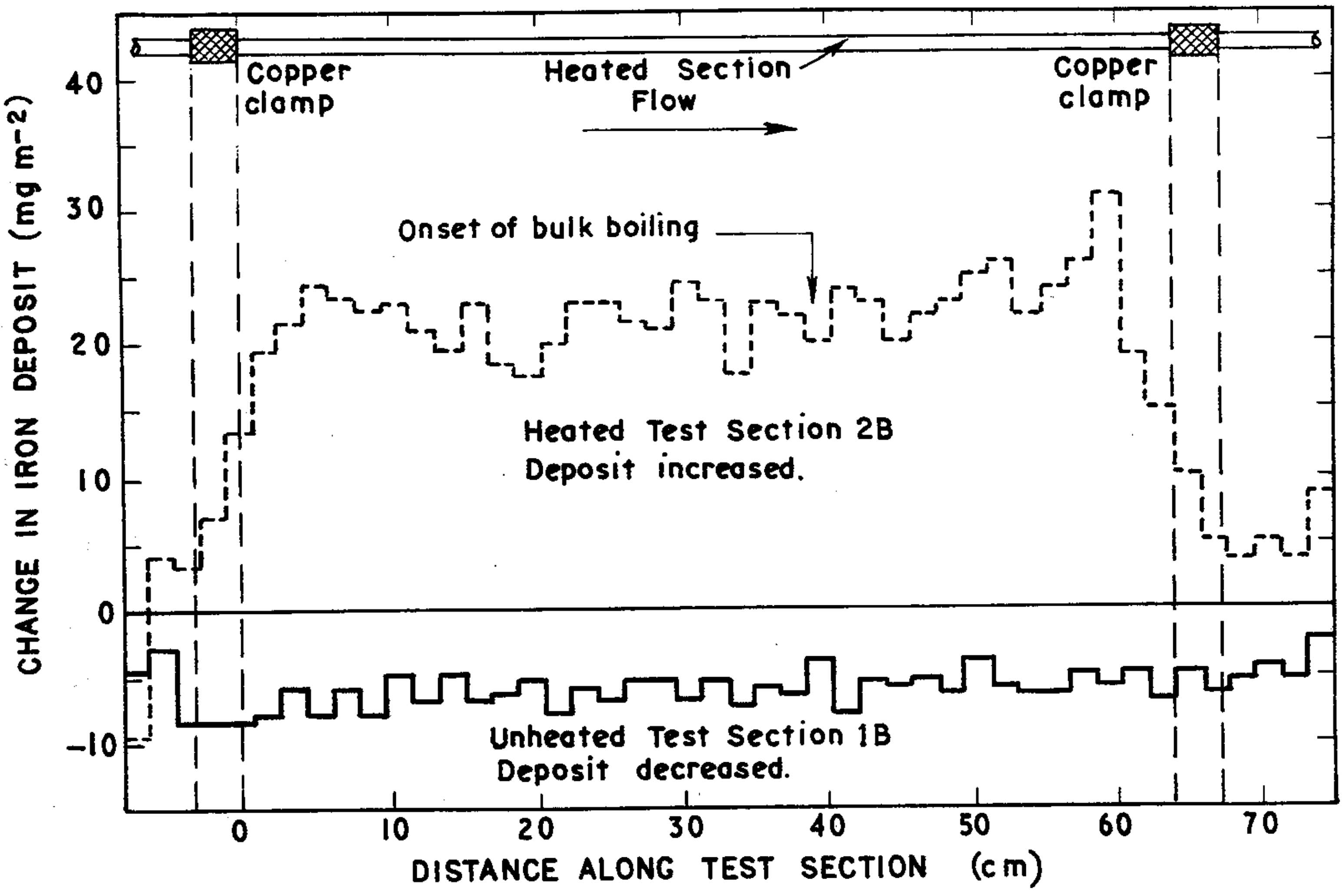
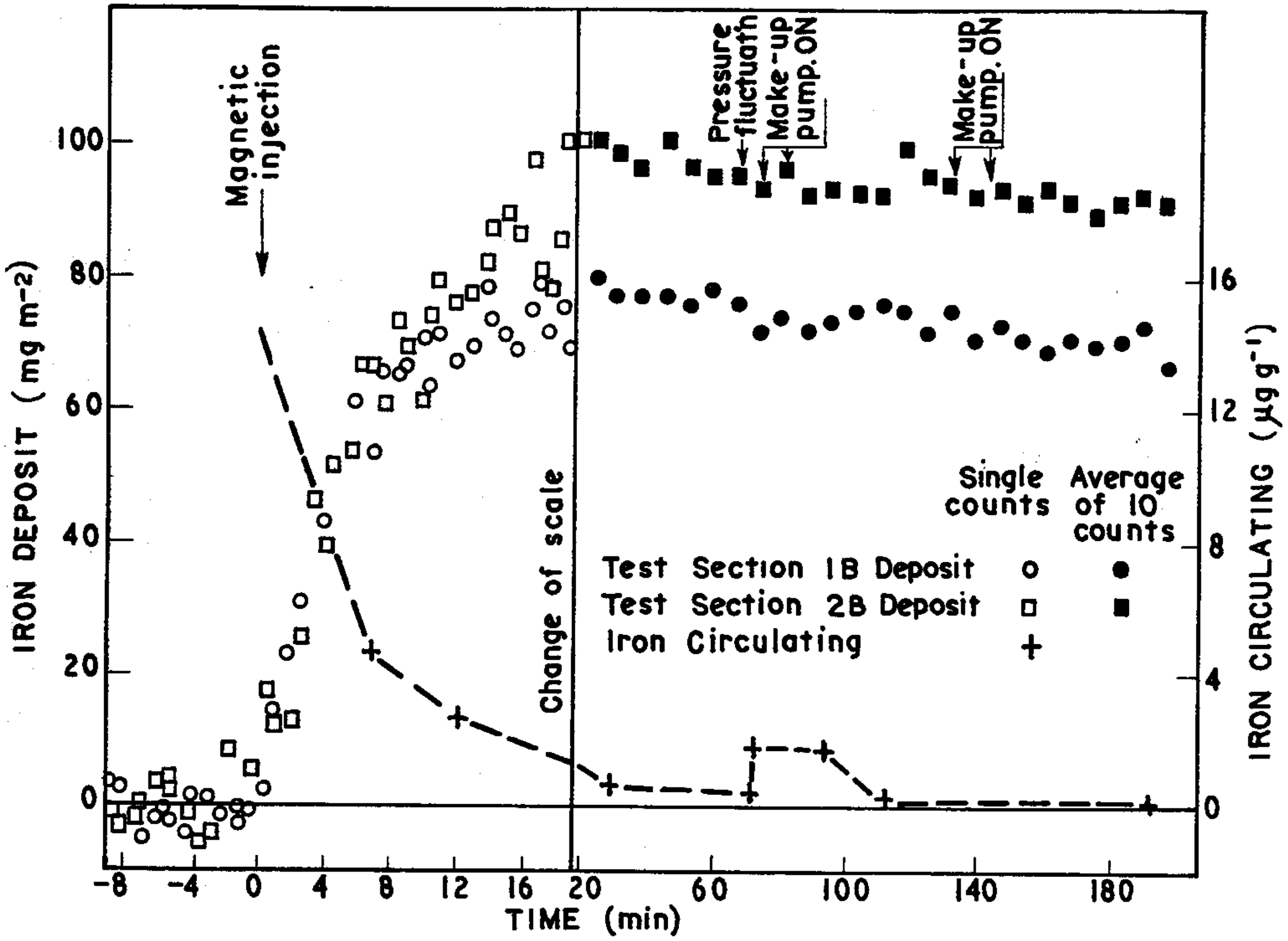


FIGURE 18. CHANGE IN DEPOSIT DURING EXPERIMENT 5



. FIGURE 19. DEPOSITION OF MAGNETITE ON THE BOILING TEST SECTIONS IN EXPERIMENT 6

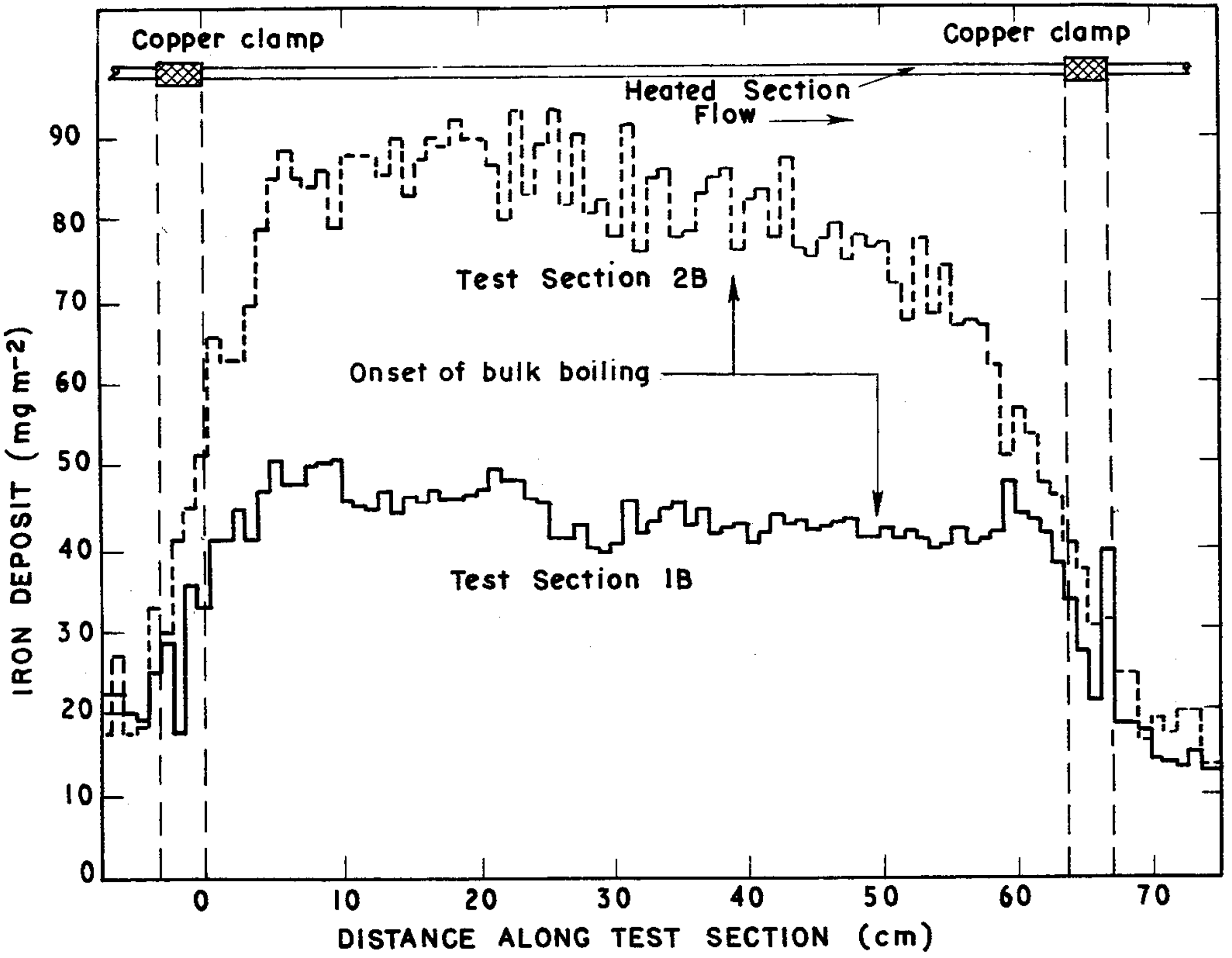


FIGURE 20. ACCUMULATED DEPOSIT FROM EXPERIMENT 6.

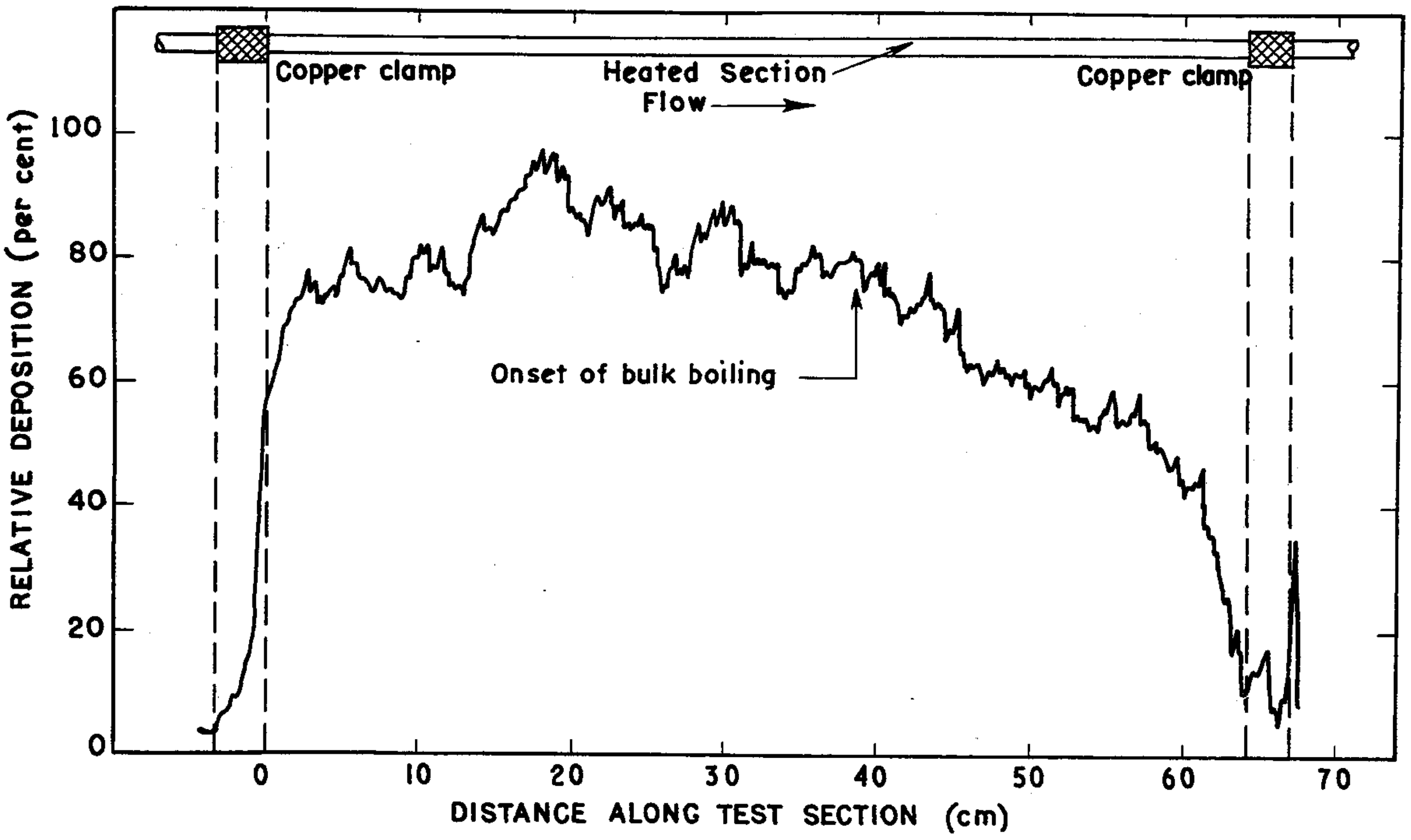
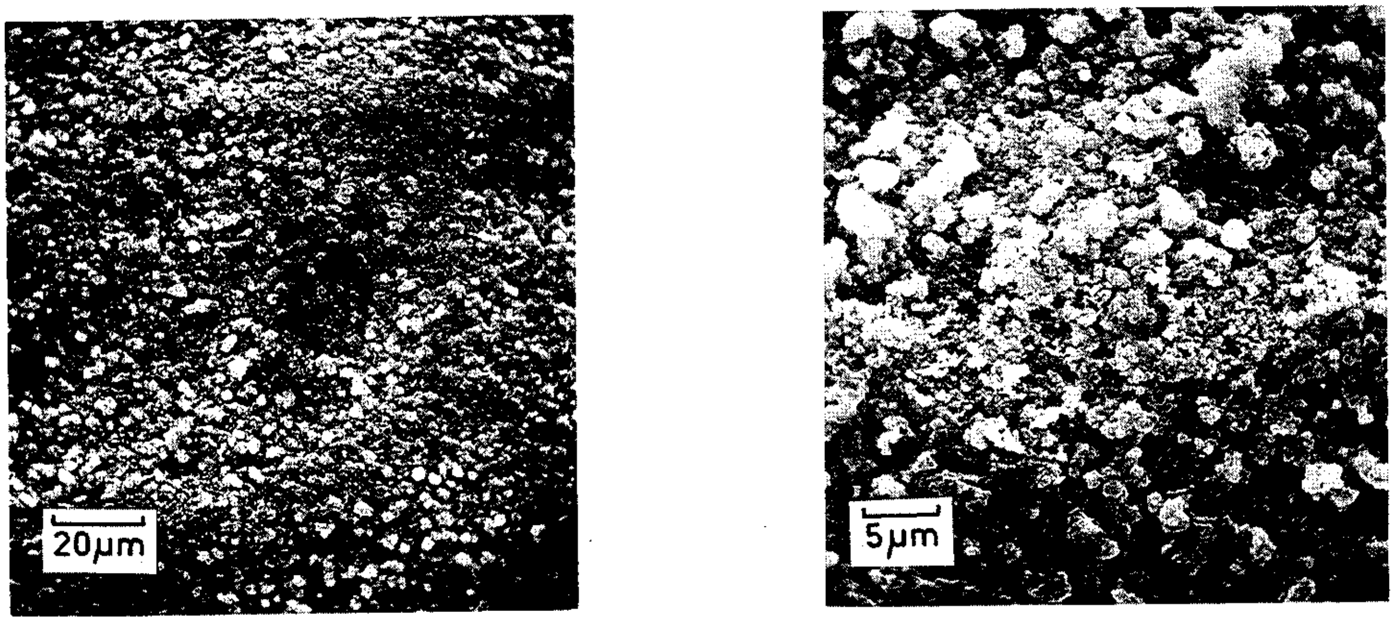


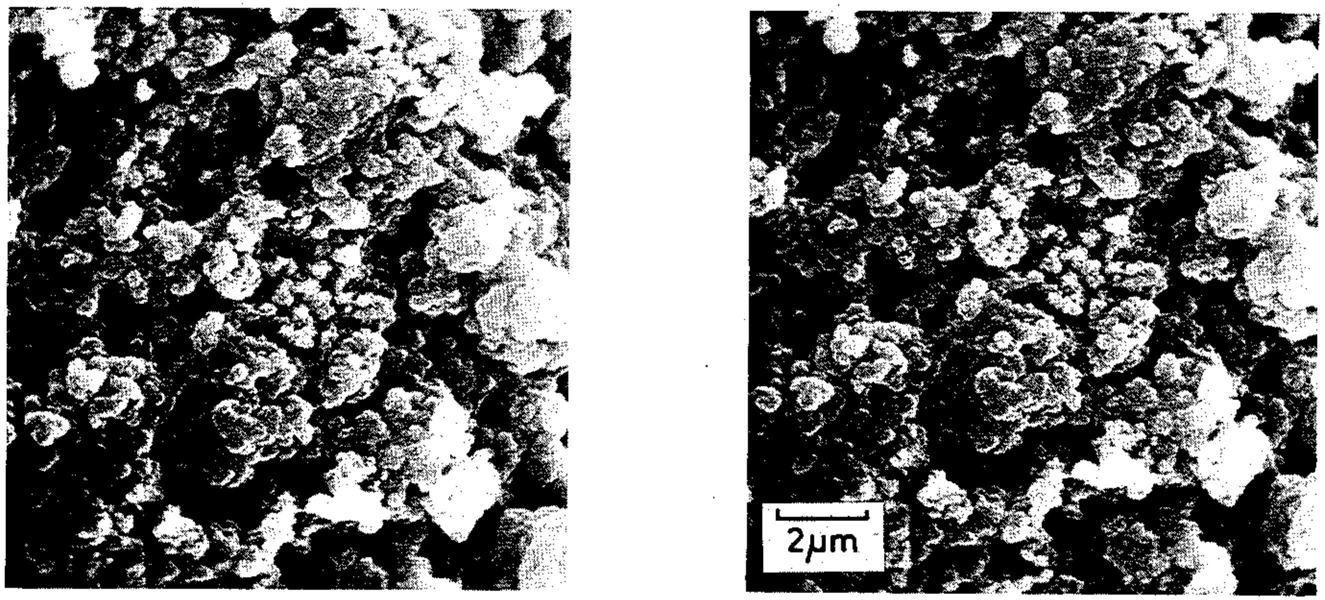
FIGURE 21. MICRODENSITOMETER GRAPH OF AUTORADIOGRAPH OF TEST SECTION 2B AFTER EXPERIMENT 6



(a) ×600

(b) × 2000

FIGURE 22. TWO SCANNING ELECTRONMICROGRAPHS OF THE SURFACE OF TEST SECTION 2B AFTER EXPERIMENT 6



×6000

FIGURE 23. A STEREO-PAIR OF ELECTRON MICROGRAPHS OF THE SURFACE OF TEST SECTION 2B AFTER EXPERIMENT 6. STEREO ANGLE 5°