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CONSTRUCTION OF A MULTICELL MICROCALORIMETER

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ABSTRACT

A very sensitive, economical, and easy to maintain multicell microcalorimeter for measurement of heat of hydration of cement and cement products has been constructed. Precision temperature control is unnecessary since each sample cell has its own reference which compensates for environmental temperature fluctuations. Ten samples can be run almost simultaneously under the same or different temperatures. The signal is a differential voltage in millivolts. A digital data recorder with a range of −2000 to +2000 mV is used, to allow the study of several samples with varying magnitudes of heats of hydration. Two reaction surfaces for the calorimeter cell were also studied in order to see their effects on the evolution of heat. A silver surface gave better results than the commonly used brass.

INTRODUCTION

A very sensitive psuedo-adiabatic multicell microcalorimeter was constructed for the purpose of measuring the heat of hydration of small amounts of cements and cement products, from 0 to 24 h after reaction with water at various reaction (hydration) conditions.

The high sensitivity is required to counteract the heat capacity effect of the reaction cell since only a fraction of the heat evolved is detected, by a conductive process. The process can be expressed by the equation:

$$\mathrm{d}Q/\mathrm{d}t = H(\mathrm{d}(\Delta T)/\mathrm{d}t) + \sigma\Delta T \qquad (1)$$

where Q = total heat evolved, H = heat capacity of the cell including the water of reaction, since it is kept constant for a series of reactions, t = time, and σ = thermal conductivity of the reaction surface material in contact with the thermistors or the heat sensors (i.e. the cell base). The heat lost, $\sigma\Delta T$, is

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the heat fraction measured and is used to follow the reaction kinetics. Expressing $\sigma\Delta T$ as a function of time, it becomes dq/dt, where $q = \sigma\Delta T$. The heat escaping from the cell, dq/dt, is used as a measure of the rate of heat evolution (rate of cement hydration) in the early stages. Cement samples as small as 0.1 g can be studied.

Since $\sigma\Delta T$ plotted as a function of time becomes dq/dt, the heat equation (1) takes the form:

$$dQ/dt = H(1/\sigma)(d^2q/d^2t^2) + (dq/dt) \tag{2}$$

where the second term in eqn. (2), $H(1/\sigma)$ (d^2q/d^2t^2), is the calorimetric constant. This second term should be constant for small temperature changes. The product of the heat capacity and the thermal conductivity, $H(1/\sigma)$, can be obtained using a material with a known heat content such as reagent grade calcium sulfate hemihydrate ($CaSO_4 \cdot 1/2H_2O$). A calibrated batch of the triclinic form of tricalcium silicate (Ca_3SiO_5) was used as the standard in this work.

Conduction calorimeters have been reported by several workers [1–4]. However, the design of these calorimeters had several limitations that prompted the need for the design or modifications described here. The limitations are listed below in brief.

(1) The sample cells were referenced to a fixed resistor. This resulted in the need to keep very close control of environmental temperature fluctuations (to within 0.2°C), since this would affect the thermistor behavior. An expensive constant-temperature room would be required for such a setup.

(2) Those workers that tried to correct the above problem ended up using one reference cell for several sample cells. This setup is all right for routinely calibrated instruments, but each cell's signal must be zeroed or balanced and calibrated against a single reference. This requires that a normalization factor for each cell and the reference be obtained. The normalization factor is then used to adjust the cell constants to enable comparison of results across cells. For kinetic studies this can be very tedious and may lead to misplaced or shifted peak maxima and minima.

(3) Only one temperature condition at a time could be studied because all the sample cells have the same reference cell, thus limiting the experimental conditions.

(4) A special multipen recorder has to be used in order to obtain all of the signals. In this type of setup the recorder has to be equipped with an operational amplifier. All of the signals have the same amplification and the recorder pens can only be set at one sensitivity per run. This limits the studies to samples that have the same thermodynamic properties. The Q_{max} values of the samples must be known, or else important data could be lost.

(5) Several trial experiments have to be run in order to determine the appropriate amount of sample and/or the right recorder settings. This results in wasted time and sample.

(6) Reaction cells were constructed out of copper or brass. Copper and zinc are soluble at high pH, forming aquo-complexes. With low magnitudes of the heat of hydration, erroneous results may be obtained. A larger sample would be required to minimize this problem.

EXPERIMENTAL

The schematic in Fig. 1 depicts the general layout of the calorimeter, showing three temperature conditions, the ten-station Wheatstone bridge, and the digital data logger/printer.

The modified instrument described here is basically composed of:

(1) Cells constructed of PVC piping material.
(2) Silver plates for a reaction surface.
(3) Yellow Springs Instruments precision thermistors (YSI 44030).
(4) A completely sealed hydration cell base.
(5) A multichannel microprocessor-controlled digital data logger capable of recording signals from −2000 to +2000 mV at one span. The data logger outputs a printed millivolt reading every second or as desired up to an interval of 24 h. The output is a listing of the day, time, the channel number, and the signal in millivolts. This allows for real time tracking of the reactions as they progress. The different reactions can start and end at the same or separate intervals. If more sensitivity is desired, each channel can be amplified separately. This is an inexpensive way to proceed. An ideal way would be to use a microcomputer equipped with a multichannel analog-to-digital signal converter for data collection and storage. This facilitates data manipulation, i.e. peak area integration, curve superimposition, and for multicomponent samples, the ability to do peak separation, or deconvolution. However, the digital data logger/printer mentioned above is sufficient for our work.

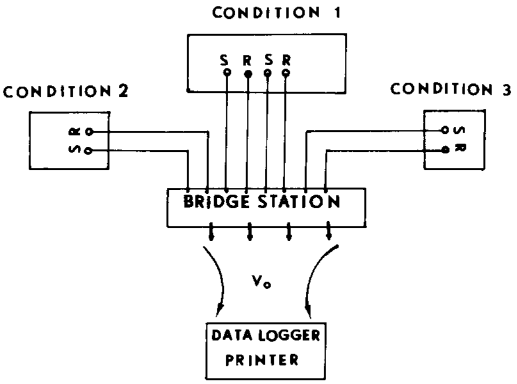

Fig. 1. A schematic of the calorimeter configurations for three temperature conditions.

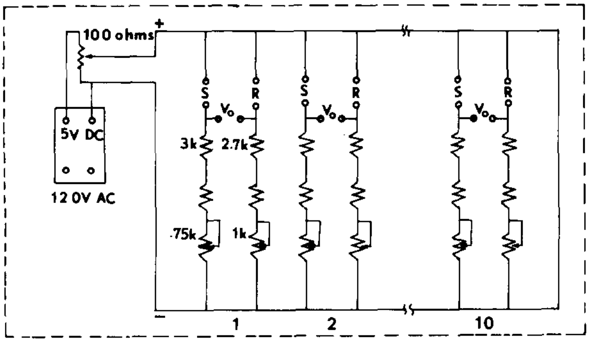

Fig. 2. Circuit architecture of the ten-station Wheatstone bridge. R = reference cells, S = sample cells.

(6) A constant dc power supply capable of varying the excitation voltage.
(7) A ten-station, single-power-supply Wheatstone bridge (Fig. 2).
(8) A water bath capable of both cryogenic and high temperature conditions.

The cell is constructed differently from the other designs mentioned above. Figure 3 shows the general construction of the reaction cell. (A) is the PVC piping which is about 1/2 in. diameter and 1/8 in. thick, it is bonded to another PVC piping of the same wall thickness and of about 3/4 in. diameter. (B) is a rubber stopper with a self-sealing septum in the middle to allow for injections of water. (C) is the silver plate, 1/32 in. thick, bonded to the inner PVC piping. (D) is the YSI 44030 thermistor, permanently attached with an epoxy binding material to the silver reaction base with a specially formulated epoxy adhesive (Eccobond 43 from the W.R. Grace Company, Cambridge, MA), which is a heat conducting but electrically insulating material. (E) is an RTV type silicon-based sealant with poor heat

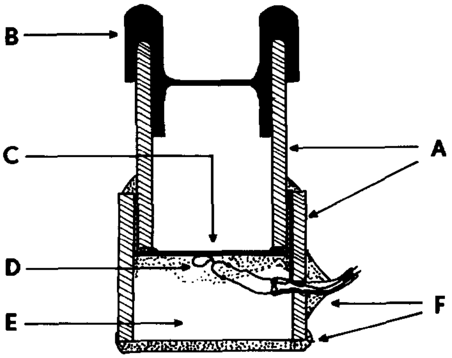

Fig. 3. The calorimeter cell showing the thermistor attached to the bottom of the reaction plate.

and electrical conductivity, it is used to fill up the space and to waterproof the thermistor wire ends. The cell base is permanently sealed with an epoxy adhesive (F).

The thermistors are initially screened for closeness in resistance. The resistances at ambient temperature are compared, then the time taken to reach a certain resistance at constant temperature is determined. Finally, the response time at changing temperature conditions (both increasing and decreasing) is obtained. Only thermistors with similar responses were used. In this work only two thermistors out of 25 were rejected. After the cells are constructed the screening procedure is repeated with each cell. In our work, only one cell out of 23 was rejected.

The calorimetric cell constant is obtained by calibration using materials of known heats of hydration to determine the cell constant. For quantitative work, three or four standards within a certain range can be used. A working curve can then be plotted to use in determining total heats of hydration. For kinetic studies of a series of materials, the calorimetric constant need not be determined since the parameters of interest are the relative heat evolution peak heights (Q_{max}) and the relative time at peak maxima (t_{max}).

The resistance to voltage conversion is achieved by the use of a ten-station Wheatstone bridge with a single power source. The power supply is a Hammond 1591-E, 5 V dc power supply model S-5-500 with a current rating of 500 mA, manufactured by Cardon Corporation of Canada. The 100 ohms variable resistor was inserted after the power supply (Fig. 3) to enable the excitation voltage to be varied with a minimum at 0 V and maximum at 5 V. The higher the excitation voltage the higher the signal (differential voltage) output by the Wheatstone bridge and vice versa, the relationship (Fig. 4) is expressed as follows:

$$V_0 = V_x - V_y = V[R_u/(R_a + R_u) - R/(R_b + R)] \tag{3}$$

where V is the excitation voltage and V_0 is the signal detected, V_x and V_y are the voltages across the sample and reference cells, respectively, R_u is the

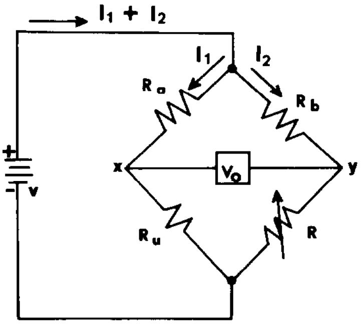

Fig. 4. A Wheatstone bridge showing the resistance-to-voltage relationship (eqn. 3).

resistance across the sample cell and R is the resistance across the reference cell. R_a and R_b are constant throughout the hydration process. When no heat is being evolved, $V_0 = 0$ and $R_u = R(R_a/R_b)$. The condition of maximum sensitivity (dV_0/dR_u) occurs when $R_u = R_a$, since

$$dV_0/dR_u = V\left[(R_a + R_u)/(R_a + R_u)^2\right] \tag{4}$$

$$= V\left[R_a/(R_a + R_u)^2\right] \tag{5}$$

From these equations it can be seen that the measured signal is the differential voltage or the voltage difference between the sample and the reference cell. This arrangement allows for corrections for environmental temperature fluctuations and power supply noise, since the reference cell signals are subtracted from the sample cell signals on line. The digital data logger acts as a null detector.

RESULTS AND DISCUSSION

Heat evolution profiles of different materials were studied. Figure 5 shows the rate of heat evolution during the hydration of tricalcium aluminate ($Ca_3Al_2O_6$). A laboratory-prepared sample (curve 1) and a commercial sample (curves 2 and 3) were used to demonstrate differences in heat evolution during hydration. The materials had similar specific surface areas, about 2500 $cm^2\ g^{-1}$, measured with the Blaine air permeability apparatus. Both samples claimed to have a free lime content of less than 0.2%. Curve 1, however, shows that sample 1 has a higher rate of heat evolution. If one accepts the fact that they both have the same particle size, particle size distribution and free lime content (and other alkali oxides), the only explanation would be differences in their thermal histories. This would pro-

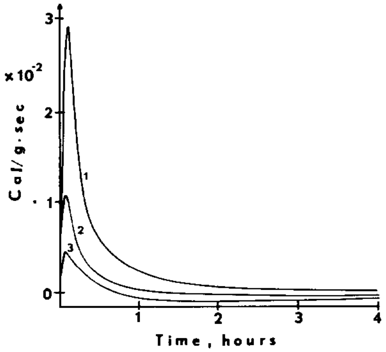

Fig. 5. Rate of heat evolution (dq/dt) of $Ca_3Al_2O_6$, W/S = 0.5. Experimental sample (1) and commercial material (2), both at 0.25 g water/0.5 g solid, and commercial material (3) at 0.13 g water/0.25 g solid.

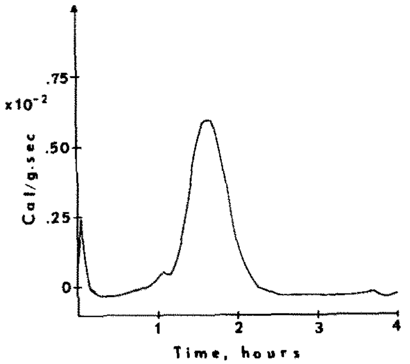

Fig. 6. A bimodal heat evolution profile of $CaSO_4 \cdot 1/2H_2O$. W/S = 0.5.

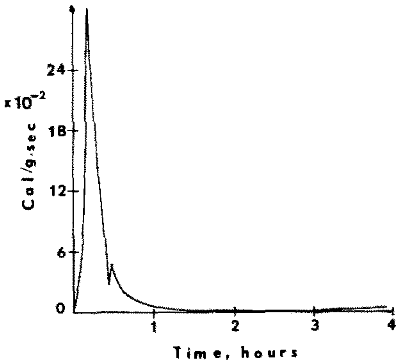

Fig. 7. Rate of heat evolution profile of freshly calcined CaO from aragonite at 1200°C. W/S = 0.5.

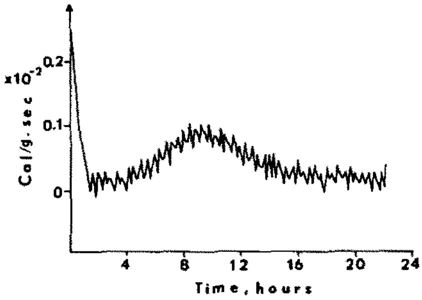

Fig. 8. Rate of heat evolution profile of Ca_3SiO_5. The baseline noise is due to secondary reactions on the brass plate (eqns. 6 and 7).

duce differences in the crystalline structures and surface energies of the materials. Curve 3 is the heat evolution of half the amount used to obtain curve 2. Q_{max} of curve 3 is half that of curve 2, accordingly. Figure 6 shows the profile of a reagent grade hemihydrate ($CaSO_4 \cdot 1/2H_2O$), a bimodal hydration profile. Figure 7 depicts the hydration profile of freshly calcined CaO, a highly exothermic reaction. All these samples were hydrated with a water-to-solid ratio (W/S) of 1 (0.5 g of solid plus 0.5 g of deionized distilled water).

The initial construction of the calorimetric cell used brass plates for the hydration surface. Figure 8 shows the output from the digital data logger of a sample hydrated in a cell with a brass hydration surface. A very low signal-to-noise ratio was observed, which was thought to be due to a leaky sample cell. However, this was observed in all such constructed cells. When silver plates were used, a smooth baseline was obtained. Examination of the surface after hydration showed the presence of a corrosion product on the

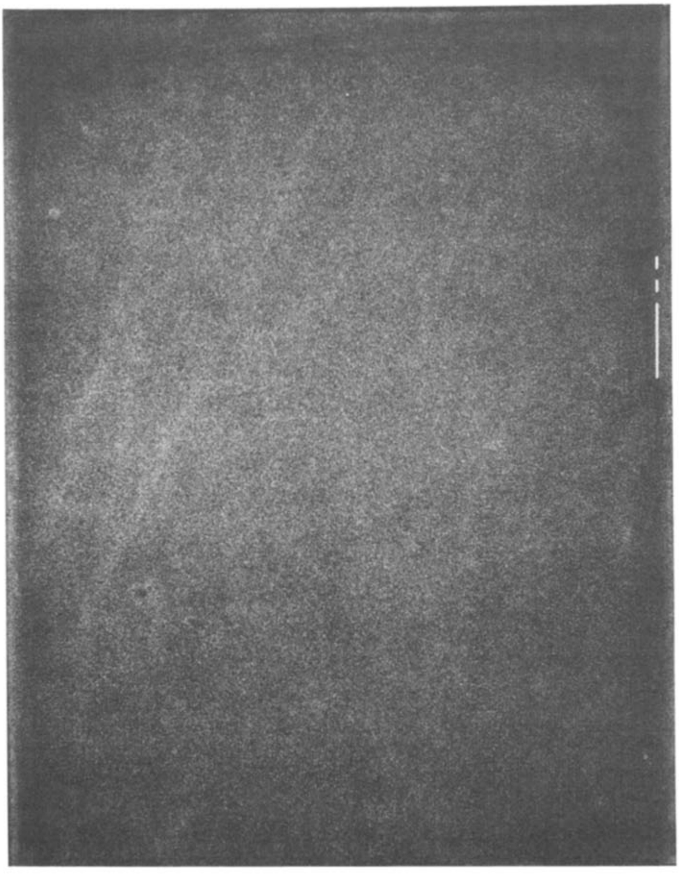

Fig. 9A. SEM micrograph (×1000) of brass surface before hydration.

surface of the brass, while the silver did not exhibit any corrosion. Figures 9A through 9D are scanning electron micrographs of the surfaces before the reaction and after 24 h hydration of Ca_3SiO_5, rinsed with dilute HCl. Pitting is observed on the brass plate (Fig. 9B) while it is almost absent from the silver plate surface (Fig. 9D). It is this corrosion reaction on the surface of the brass plate which we believe is responsible for the rough baseline in Fig. 8. The possible reactions are probably those shown in eqns. (6) and (7) [5]

$$CaO + Cu + H_2O = Ca(Cu(OH)_4) \tag{6}$$

and

$$CaO + Zn + H_2O = Ca(Zn(OH)_4) \tag{7}$$

CONCLUSION

The special features of this multicell microcalorimeter are:

(1) The use of one constant voltage power supply for the ten-station

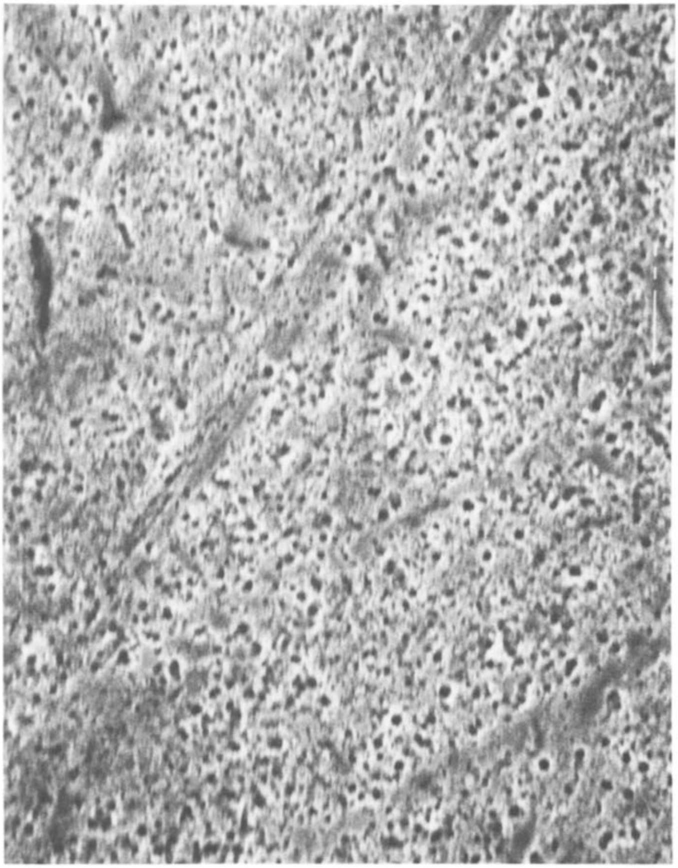

Fig. 9B. SEM micrograph (×1000) of brass surface after hydration of Ca_3SiO_5, $W/S = 0.5$.

Wheatstone bridge capable of supplying stable excitation voltages from 0 to 5 V dc. This provides a compact setup and reliable excitation voltages.

(2) The use of one reference cell per sample cell. This configuration enables one to perform the experiment at several different conditions at the same time, i.e. at ambient temperature and at whatever temperature the water bath is set, since a reference exists for each condition. Close temperature control is not necessary.

(3) An inexpensive programmable multichannel digital data logger with real time printed output per channel and capable of one reading every second with a recording span of −2000 to +2000 mV. Although a microcomputer could be used, the frequency of data collection in these experiments does not warrant one. The cost of an analog-to-digital converter for interfacing with a microcomputer is equivalent to the cost of the digital data logger.

(4) The use of a silver reaction surface improves the sensitivity and

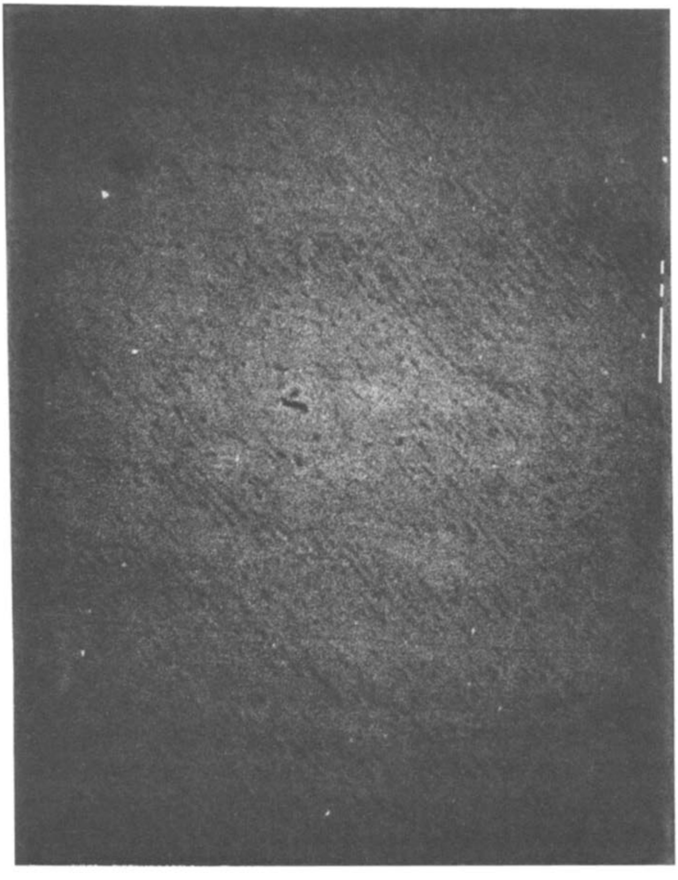

Fig. 9C. SEM micrograph (×1000) of silver surface before hydration.

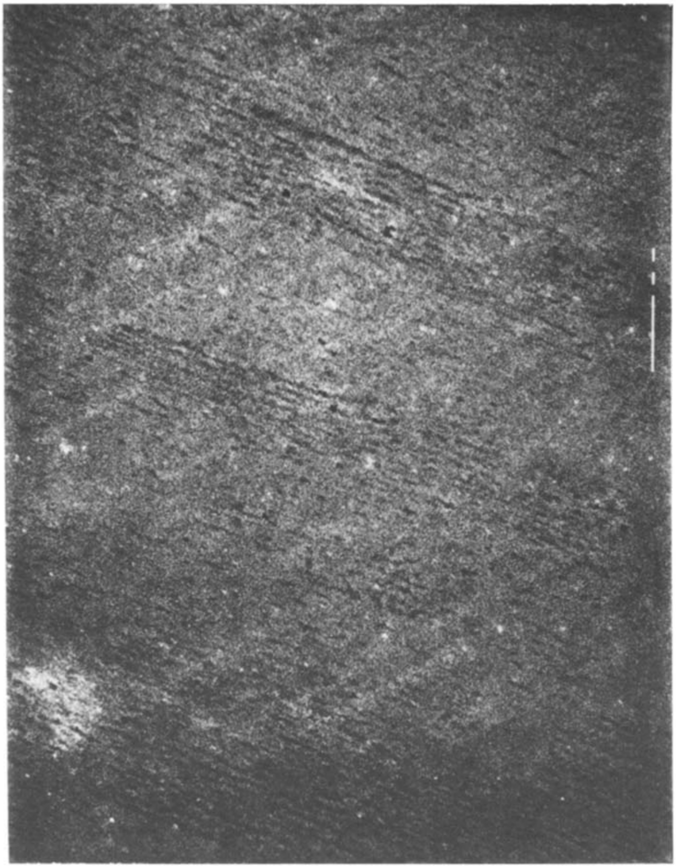

Fig. 9D. SEM micrograph (× 1000) of silver surface after hydration of Ca_3SiO_5, W/S = 0.5.

reliability of such calorimeters. Silver is advantageous since it is not prone to corrosion (as is brass) and it is a better heat conductor.

The only known disadvantage is that kinetic work may have to be limited to the low-heat-generating samples. The rate of heat transfer could reach a maximum heat transfer flux of the cell base plate material and the linearity of Q_{max} would be lost. This has not been observed in our work. However, the problem could be remedied by reducing the sample size accordingly.

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