APPENDIX 7.3

CALCULATION OF THE CONTRIBUTION OF H_2S OXIDATION

TO THE OXIDATION OF CuS.

An estimate of the possible contribution of this mechanism

of oxidation to the total bacterial metabolism can be

calculated from the following information;

   a. The thermodynamic data of Wagman et al. (1968 & 1969)

together with the data of Barton (1973) allows calculation

of the maximum [H_2S] compatible with given pH and [Cu^{2+}].

Eq. 7.3.1 $\log[H_2S] = -15.6 - 2pH - \log[Cu^{2+}]$ at 25°C.

                  (concentrations in mol l^{-1})

   b. McLaren and Packer (1970) review the encounter

rate theory of Smoluchowski which allows calculation of

the maximum rate of H_2S uptake at the above concentration.

Eq. 7.3.2   Encounter rate = 4π R D[H_2S] molecules/sec

                  where R = radius of a cell,(cm),

                     D = Fick's self diffusion
                        coefficient for H_2S
                        (cm^2/sec), and [H_2S] is in
                        molecules per ml.

Data from Perry and Chilton (1973), suggests

$D(H_2S) = 1.2 \times 10^{-5} cm^2$/sec.

   c. Page 3 of Meynell and Meynell (1970) states that

10^9 Gram negative bacteria contain 300 µg dry weight. If

1/3 of this is carbon, then each cell requires 5×10^9

carbon atoms to reproduce itself. In Appendix 7.2 it is

shown that for every 12 carbon atoms fixed, at least 100

sulphur atoms are oxidized. Since each sulphur atom is

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equal to six reducing equivalents the number of

reducing equivalents required by each cell to reduce

a CO_2 molecule is $\frac{6 \text{ X } 100}{12}$ = 50.

Therefore, to reproduce itself, each cell must oxidize

$2.5 \text{ X } 10^{11}$ reducing equivalents, or $3 \text{ X } 10^{10}$ molecules

of H_2S. (There are 8 reducing equivalents per H_2S

molecule.)

At pH 2.5 and 10^{-4} M Cu^{2+},

$\log[H_2S]$ = -15.6 -5.0 +4 = -16.6   (See Eq. 7.3.1).

i.e., $[H_2S]$ = $2.5 \text{ X } 10^{-17}$ mol l^{-1} = $1.5 \text{ X } 10^4$ molecules/ml

Assuming R = 10^{-4} cm

Encounter rate = 4π X $1.2 \text{ X } 10^{-5}$X 10^{-4}X $1.5 \text{ X } 10^4$
molecules sec^{-1}

= $2 \text{ X } 10^{-4}$ molecules sec^{-1}

Therefore the time required for each cell to double using

CuS generated H_2S as the sole substrate would be at least

$\frac{3 \text{ X } 10^{10}}{2 \text{ X } 10^{-4}}$ sec.   = 5 million years.

Obviously this mechanism makes no contribution to CuS

oxidation although it may be important for other

sulphides.

APPENDIX 7.4

CALCULATION OF THE CONTRIBUTION OF Cu^+ TO

BACTERIAL OXIDATION OF CuS.

The method of calculation is the same as used in

Appendix 7.3 and the sources of data are the same.

The maximum $[Cu^+]$ compatible with CuS, S and a given

$[Cu^{2+}]$ is;

Eq.7.4.1 $\log[Cu^+] = -7.5 + \frac{1}{2}\log[Cu^{2+}]$ (concentrations

in mol l^{-1}) at 25°C

A method of estimating the self diffusion coefficients

of ions is given in Perry and Chilton (1973). In this case

there is no nett movement of anions but only a

countercurrent movement of Cu^+ and Cu^{2+}. (The diffusion

of H^+ into the cell, necessary for stoichiometry, should

not be rate limiting, given the high mobility of H^+ in

water). For the purposes of the calculation Cu^{2+} is

treated as the anion accompanying Cu^+. The result is;

$D(Cu^+, Cu^{2+})$ = 1.1×10^{-5} cm^2 sec^{-1}.

To reproduce itself, each cell must oxidize at least

2.5×10^{11} Cu^+ ions.

At 10^{-4}M Cu^{2+}, $\log[Cu^+] = -7.5 - 2 = -9.5$ (See Eq. 7.4.1).

i.e., $[Cu^+] = 3 \times 10^{-10}$ mol $l^{-1} = 2 \times 10^{11}$ molecules/ml

Encounter rate $= 4\pi \times 10^{-4} \times 1.1 \times 10^{-5} \times 2 \times 10^{11}$ molecules sec^{-1}

$= 3 \times 10^3$ molecules sec^{-1}.

Therefore the time required for each cell to double using

Cu^+ produced by CuS would be at least $\dfrac{2.5 \times 10^{11}}{3 \times 10^3}$ sec

$= 3$ years.

This mechanism, therefore, makes no contribution to CuS

oxidation. However, if a complex were present which

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stabilized Cu^+, such that its concentration rose to 3×10^{-7} mol l^{-1}, then the cyclic oxidation and reduction of cuprous and cupric ions could lead to a doubling time of one day, which is about the observed doubling time.