COMPUTATIONAL METHODS FOR ESTIMATING PRECIPITATION FROM GEOTHERMAL BRINES

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Laboratory experiments using Salton Sea Geothermal Field brines at elevated temperatures are costly, time-consuming, and potentially difficult to perform. The LLL Geothermal Program is therefore also attempting to predict equilibria in the SSGF brines by computation.

Two approaches to this problem are being taken. Modeling of chemical reactions in the brines is being carried out using the Helgeson-Herrick (HH) code. In addition, the precipitation of many solids is being studied individually using effective activity coefficients which take chloride complexing into account.

The results of both methods are consistent with one another in predicting precipitation behavior in the temperature range 100-300°C. For example, results for Sinclair No. 4 brines at 200°C indicate that at low pH, SiO_2, MnO_2, and Fe silicates precipitate. As pH increases, Cu and Fe sulphides, Fe silicates and Fe oxides also precipitate.

For the San Diego Gas and Electric Magmamax brine at 200°C, the HH code predicts results quite similar to those described above for the Sinclair No. 4 brine with one notable exception, PbS precipitated at pH greater than 4.0. This correlates with observations on the scale examined from the San Diego Gas and Electric test site.

DISCLAIMER

BRINES ARE COMPLICATED

- Many Constituents
- Concentrated Salt Solutions
- Many Interdependent Equilibria
- Expensive to Experiment
- Scale Forming Components

LLL PROPOSED SCALE CONTROL METHODS

- Reduced pH (e.g., add HCl)
- Oxidize (e.g., S^{-2} to S)
- Combination

CODES HELP SCREEN CONTROL METHODS

- Minimize Costly Experiments
- Save Tedious Hand Calculations
- Parameter Studies of Additives
- Account for Differences between Wells

LLL USES TWO CALCULATIONAL APPROACHES

- Helgeson-Herrick Code

  Large Scale Geochemical Equilibrium Code

- Individual Solids Code

  Includes Activity Coefficient for Complexes in Concentrated Cl Solns.

Results are Mutually Consistent.

THERMOCHEMICAL CALCULATIONS

1. An approximate, or "limited reaction" method has been developed to study the chemistry of geothermal brines.

2. This method is based on the use of effective activity coefficients which take into account chlorine complexing.

3. Solubilities of scale-forming substances and distributions of non-condensable gases can be computed.

4. The effects of pH and temperature on scaling can be studied.

5. It may be possible to predict which solids will precipitate, and how much can form under specified conditions.

MINERAL SPECIES

$Fe_3Si_4O_{10}(OH)_2$	minnesotaite (talc)	$Mg_3Si_4O_{10}(OH)_2$	talc
Fe_2SiO_4	fayalite	$MgSiO_3$	eustatite
Mg_2SiO_4	forstersite	$CaFeSi_2O_6$	hedenbergite
$CaMgSi_2O_6$	diopside	$CaSiO_3$	wollastonite
MnO_2	pyrolusite	$Mg(OH)_2$	brucite
$Mg_6Si_4O_{10}(OH)_8$	serpentine	$Fe_6Si_4O_{10}(OH)_8$	greenalite
MgO	periclase	$Ca(OH)_2$	portlandite
$Ca_2Mg_5(Si_8O_{22})(OH)_2$	tremolite	$Ca_3Fe_2(SiO_4)_3$	andradite
Fe_3O_4	magnetite	Fe_2O_3	haematite
$CaSO_4$	anhydrite	$CaSO_4 \cdot 2H_2O$	gypsum
$MgFe_2O_4$	magnesioferrite	β-Ca_2SiO_4	larnite
$Mg_4(Si_6O_{15})(OH)_2 \cdot 6H_2O$	sepiolite	$Ca_2MgSi_2O_7$	ackermanite
$Ca_3MgSi_2O_8$	marwinite	$Ca_2Al_2SiO_7$	gehlenite
$CaMgSiO_4$	monticellite		
FeS	pyrrhotite	PbS	galena
CuS	covellite	Cu_2S	chalcocite
FeS_2	pyrite	ZnS	sphalerite
$CuFeS_2$	chalcopyrite	Cu_5FeS_4	bornite
Ag_2S	argentite	Cu_9S_5	digenite
NiS	millerite	HgS	cinnabar

BRINE CONDITIONS

	OXIDIZING	REDUCING
SO_4^{-2}	2.4×10^{-4} m	1×10^{-30} m
S^{-2}	1×10^{-30} m	2.4×10^{-4} m

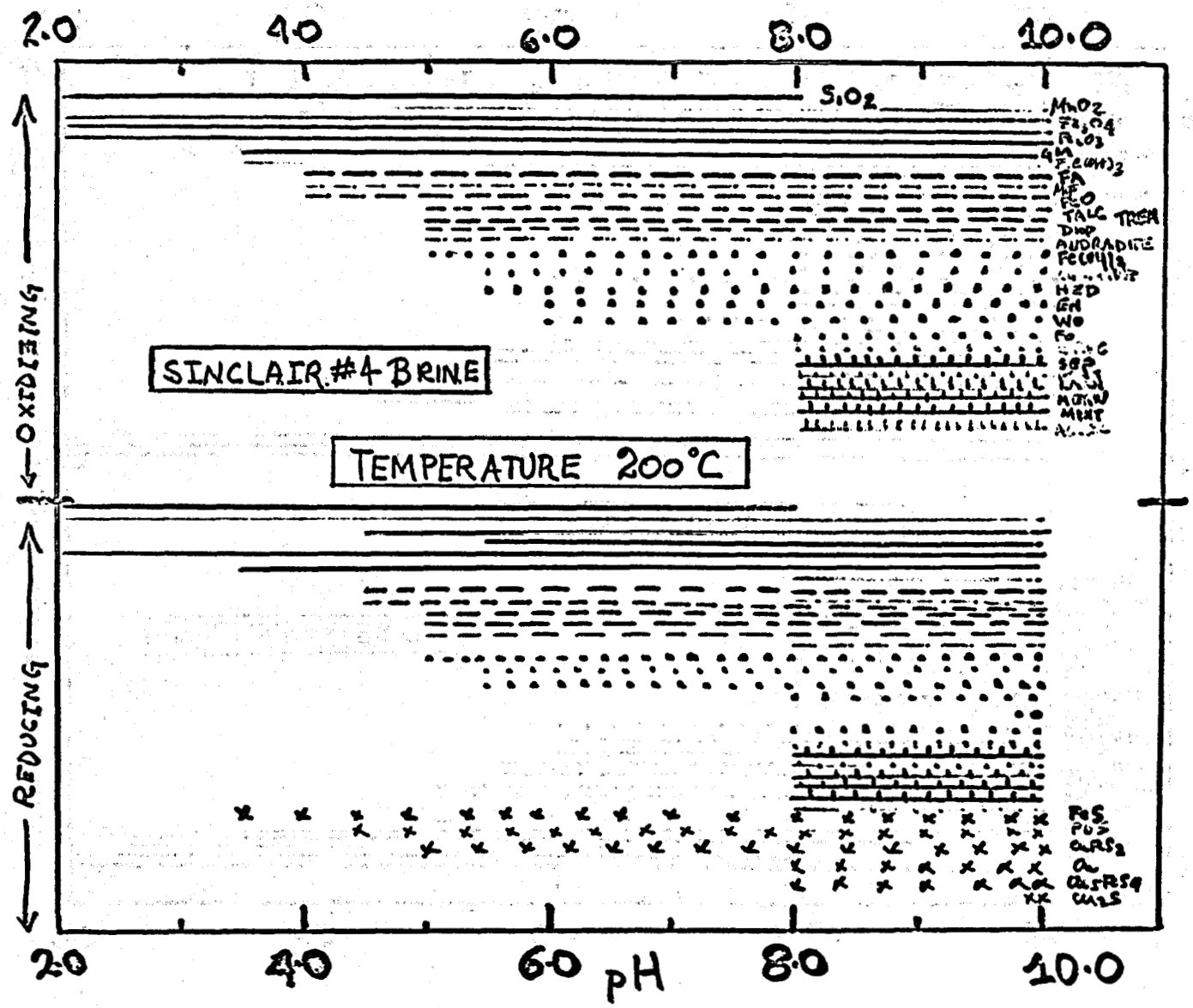
ESTIMATED CHEMICAL DATA FOR SINCLAIR 4

RESERVOIR FLUID COMPOSITION

	SPECIES	PPM	MOLS/ KG FLUID	MOLS/ KG WATER
1	AL	2.000E+00	7.412E-05	9.515E-05
2	NH4			
3	SB			
4	AS			
5	BA			
6	B			
7	BR			
8	CA	2.250E+04	5.614E-01	7.206E-01
9	CS			
10	CL	1.300E+05	3.667E+00	4.707E+00
11	CO2	4.000E+03	9.089E-02	1.167E-01
12	CU	3.000E+00	4.721E-05	6.061E-05
13	F			
14	I			
15	FE	1.150E+03	2.059E-02	2.643E-02
16	PB	7.800E+01	3.765E-04	4.833E-04
17	LI			
18	MG	5.900E+01	2.427E-03	3.115E-03
19	MN	9.500E+02	1.729E-02	2.220E-02
20	NO3			
21	K	1.160E+04	2.967E-01	3.808E-01
22	RB			
23	SIO2	4.213E+02	7.012E-03	9.001E-03
24	AG	5.000E-01	4.635E-06	5.950E-06
25	NA	5.070E+04	2.205E+00	2.831E+00
26	SR			
27	SO4	1.798E+02	1.872E-03	2.403E-03
28	S	6.000E+00	1.871E-04	2.402E-04
29	ZN			
30	TDS	2.170E+05		
31	PH	5.500E+00		

EQUILIBRIUM PARAMETERS

TEMPERATURE	F		3.740E+03
	C		1.[illegible]E+02
	K		4.[illegible]E+02
PRESSURE,	PSIA		1.70[illegible]E+02
	ATM		1.217E+01
	MPA		1.[illegible]E+00
STEAM QUALITY			1.[illegible]37E+01
MASS DISTRIBUTION/KG FLUID			
VAPOR			
	STEAM	MOLS	7.542E+00
		KG	1.357E-01
	CO2	MOLS	9.007E-02
		KG	4.000E-03
		ATM	1.437E-01
	H2S	MOLS	1.816E-04
		ATM	2.696E-04
	TOTAL	MOLS	7.633E+00
LIQUID			
	WATER	MOLS	3.574E+01
		KG	6.433E-01
	TDS	KG	2.170E-01


2.0
4.0
6.0
8.0
10.0
SiO2
MnO2
Fe3O4
Fe2O3
Fe(OH)3
FA
AHE
FEO
TALC
TREM
DHP
ANDRADITE
HED
EN
WO
FO
SINCLAIR #4 BRINE
TEMPERATURE 200°C
OXIDIZING
REDUCING
FeS
FeS2
Cu2S
CuFeS2
CuS
pH

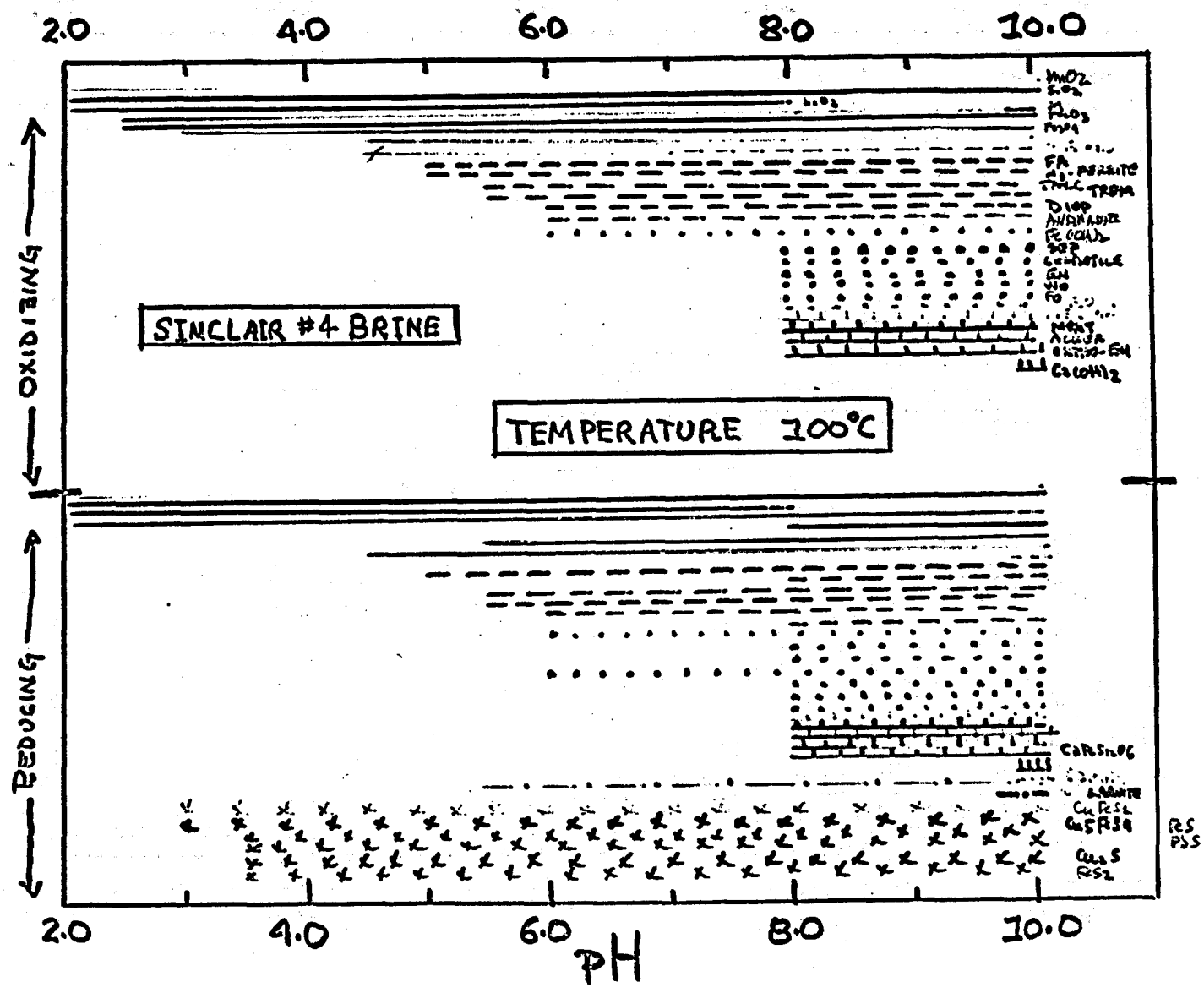

2.0
4.0
6.0
8.0
10.0
SINCLAIR #4 BRINE
TEMPERATURE 100°C
OXIDIZING
REDUCING
pH

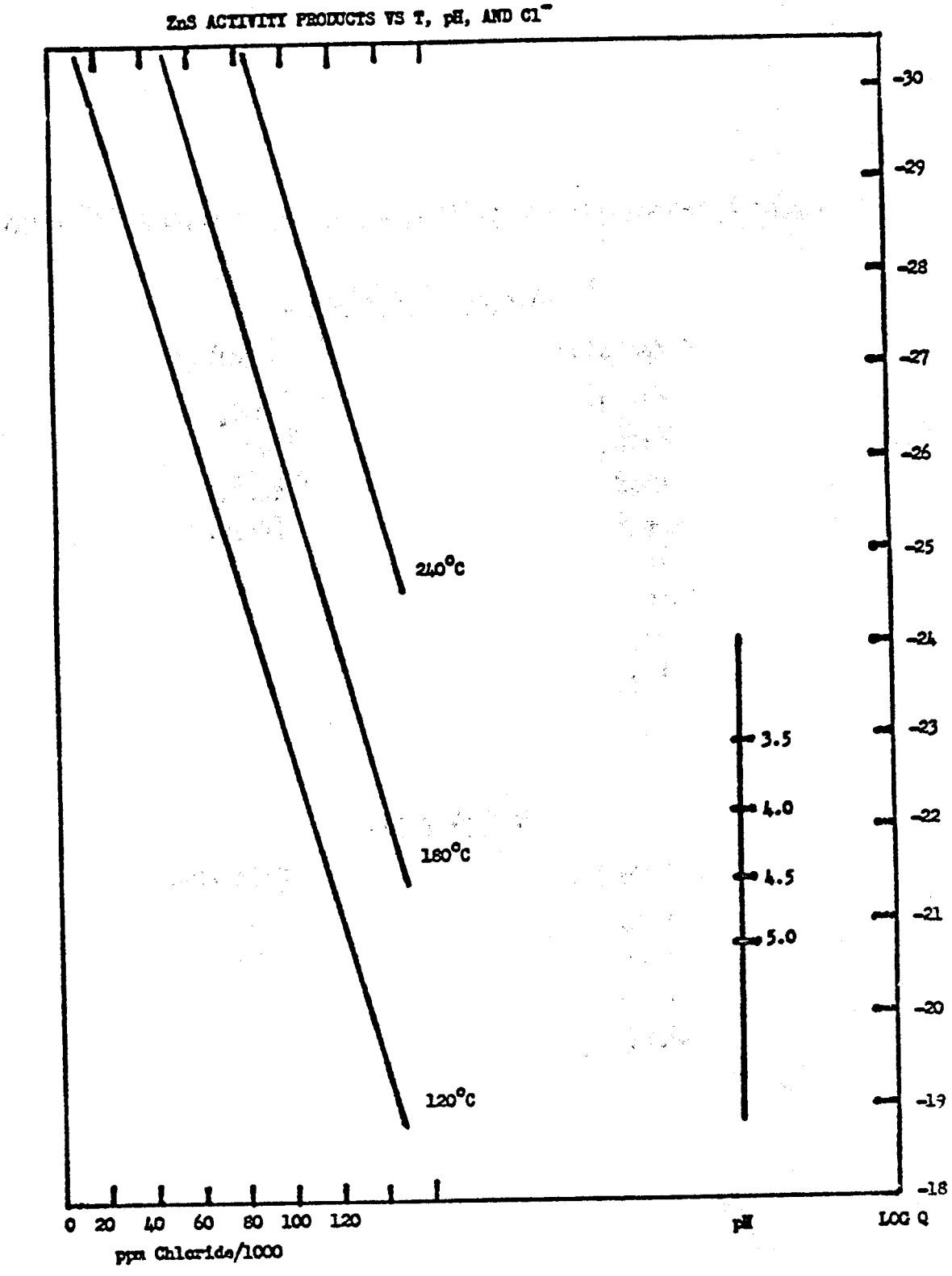
Table 1. Potential for Scale Formation from Magmamax #1 Brine

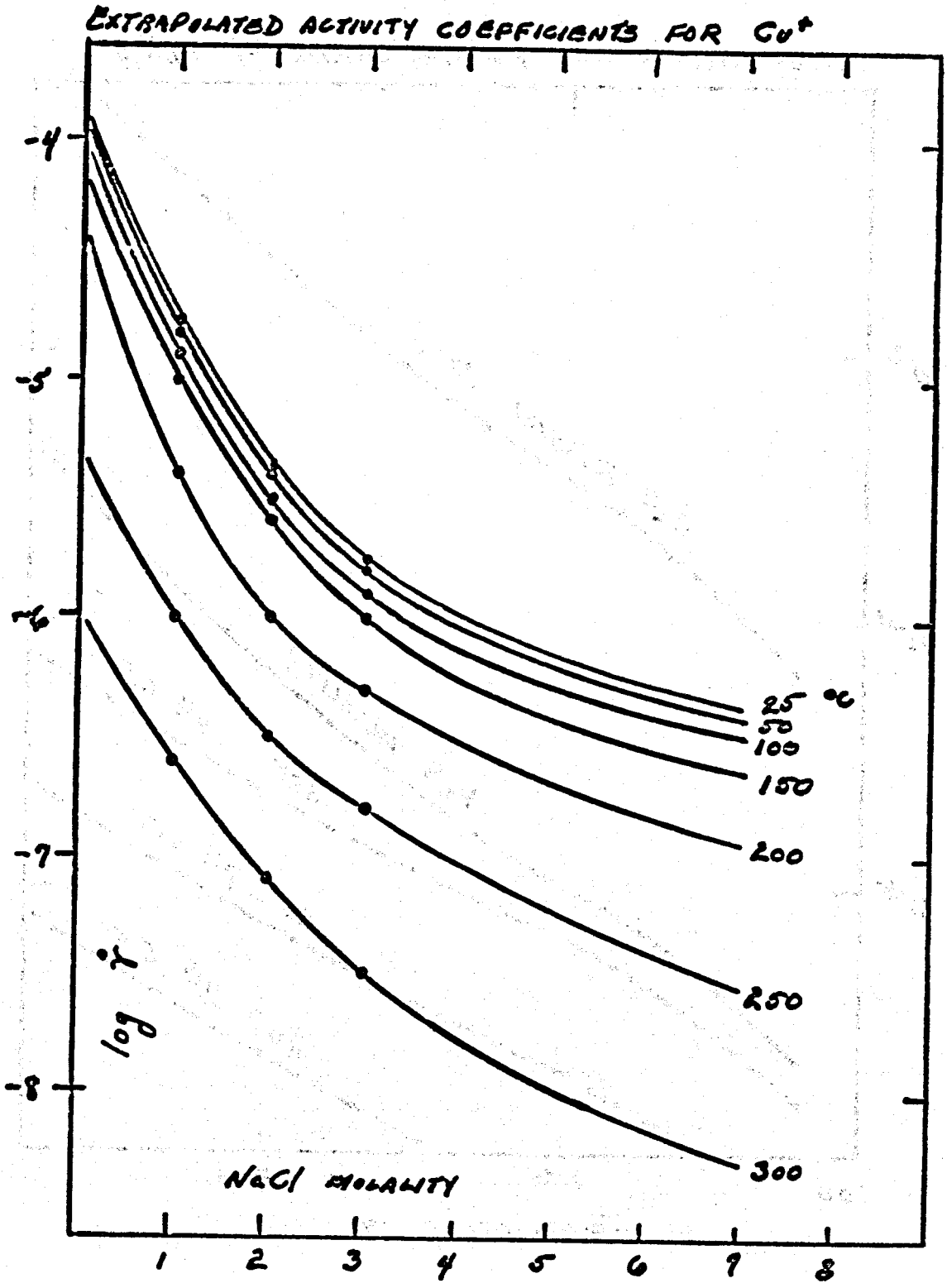
Possible Precipitation

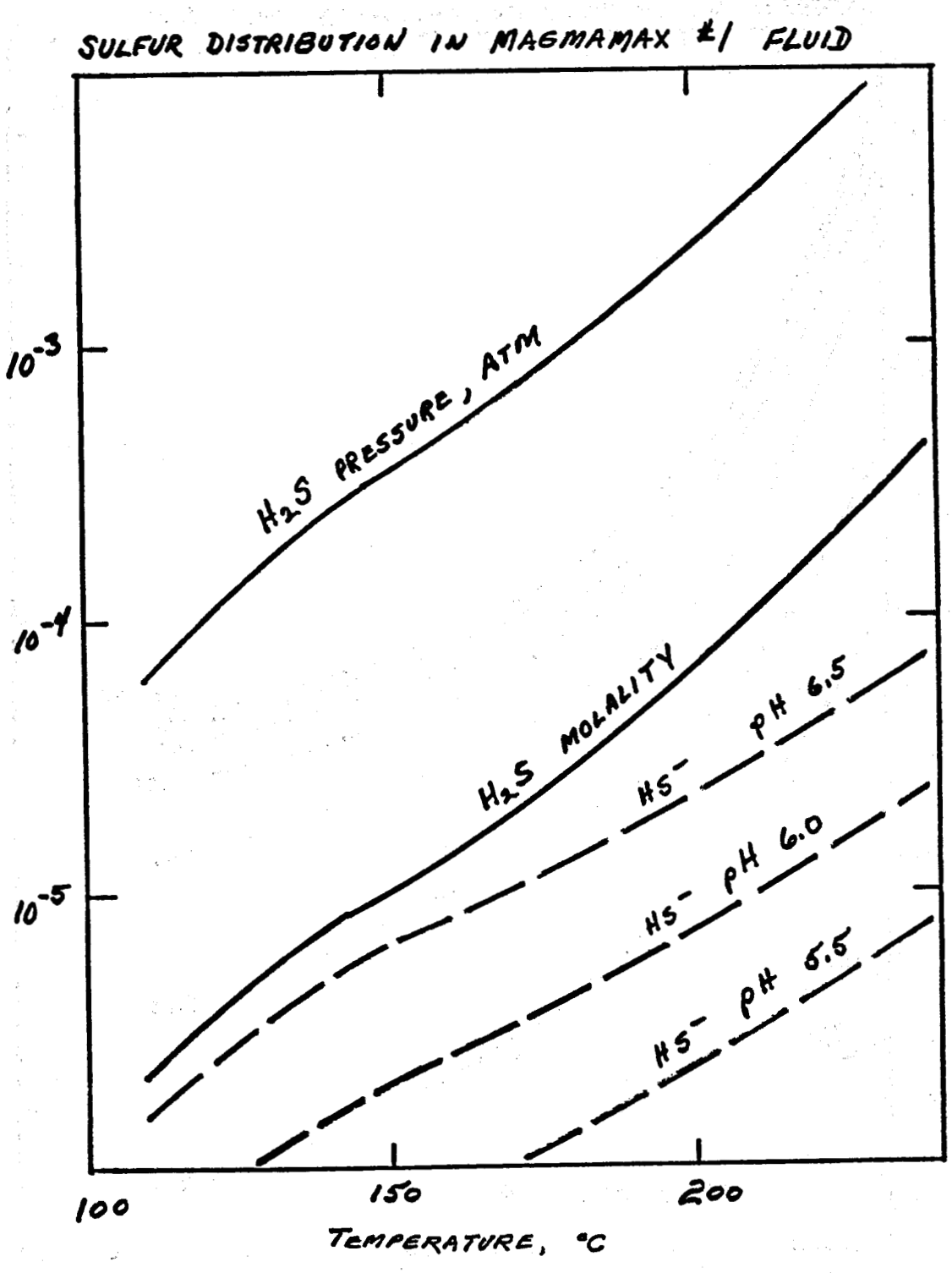
Reducing	Oxidizing
$Al(OH)_3$	Fe_2O_3
$CaCO_3$	CuS
Cu_2S	$CaSO_4$
Ag_2S	$CuFeS_2$
ZnS	
PbS	
FeS	
SiO_2	

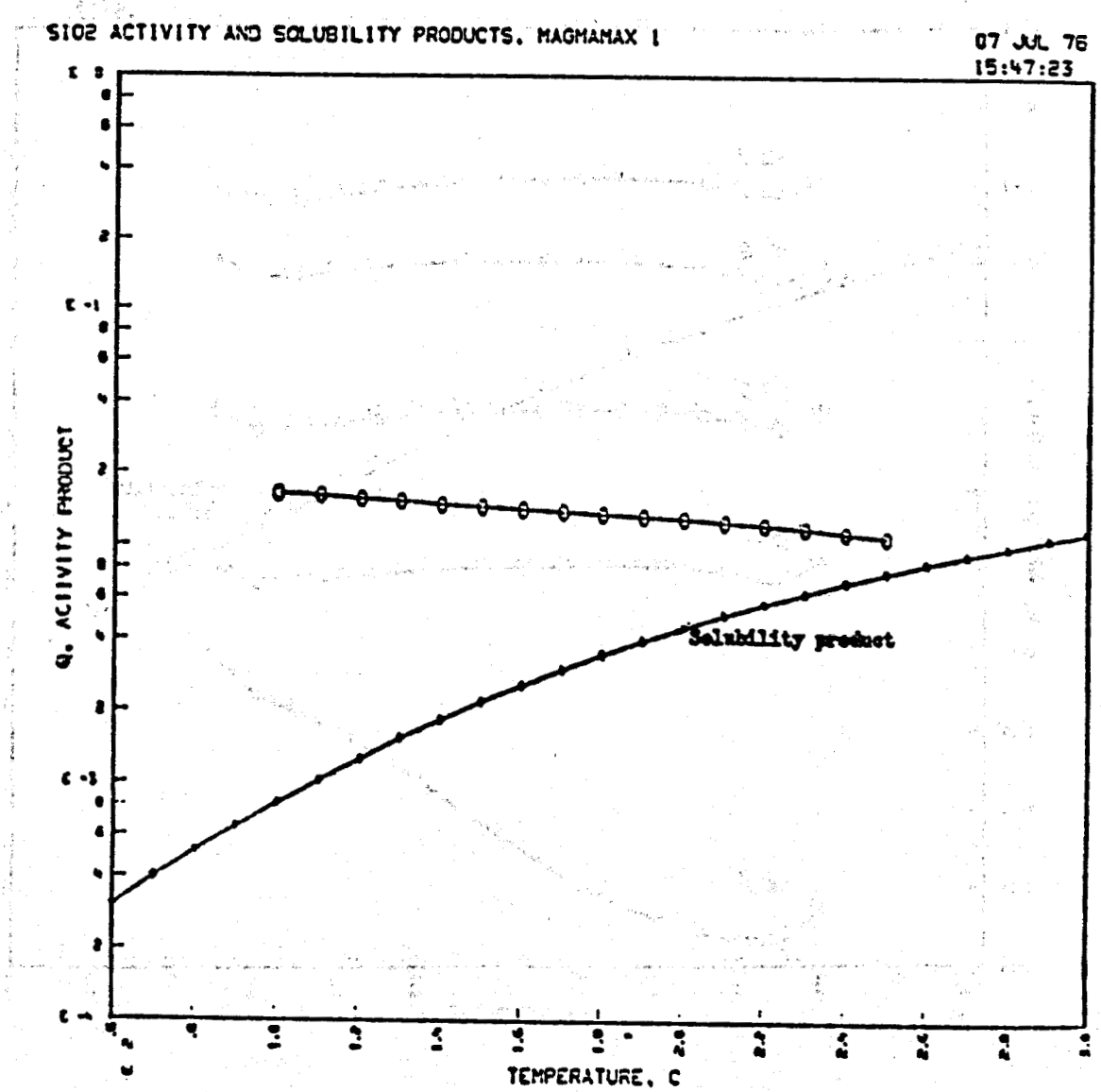
No Precipitation

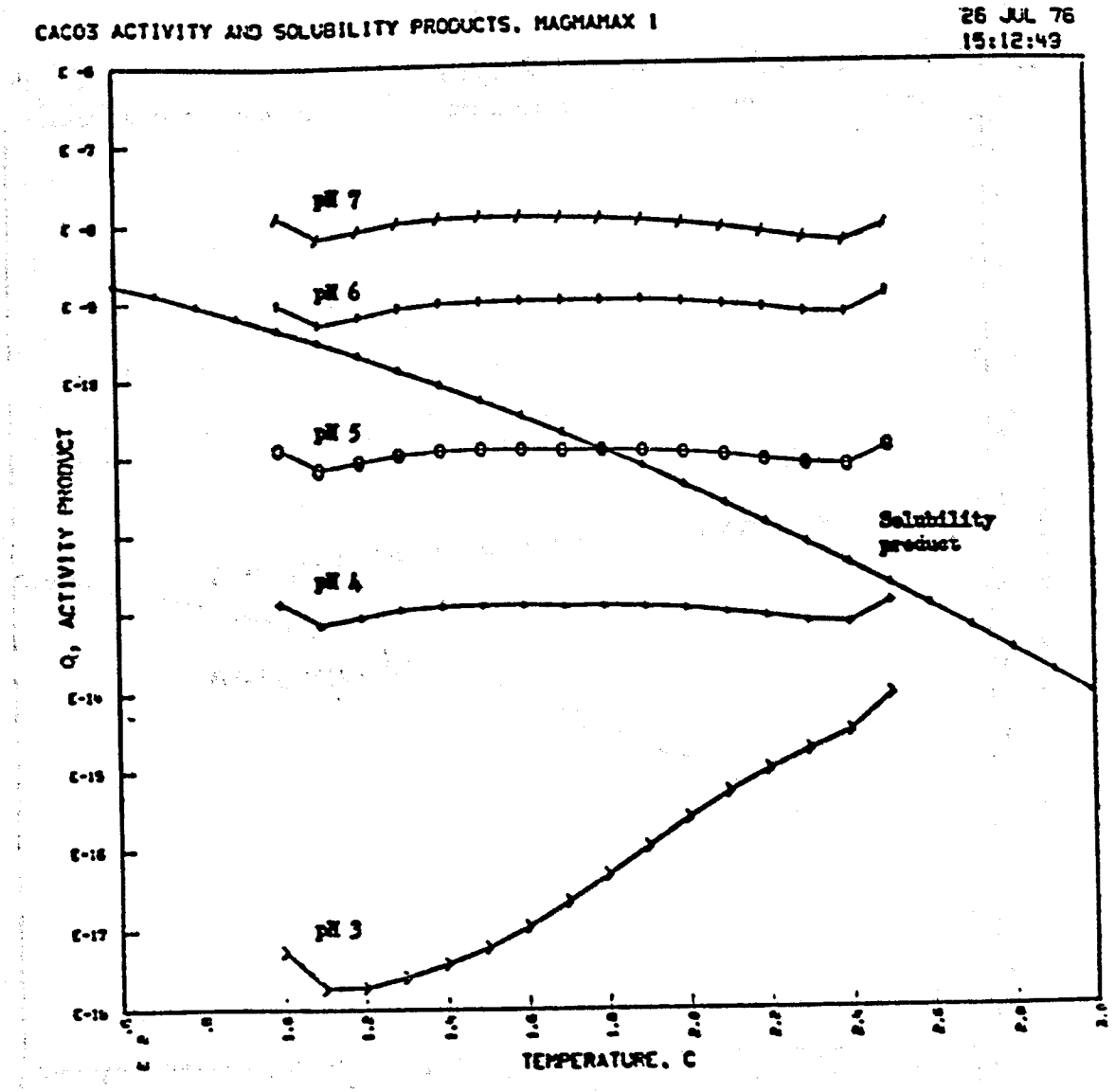
Reducing	Oxidizing
$PbCO_3$	CuO
$ZnCO_3$	$PbSO_4$
Cu_2O	
$Mg(OH)_2$	

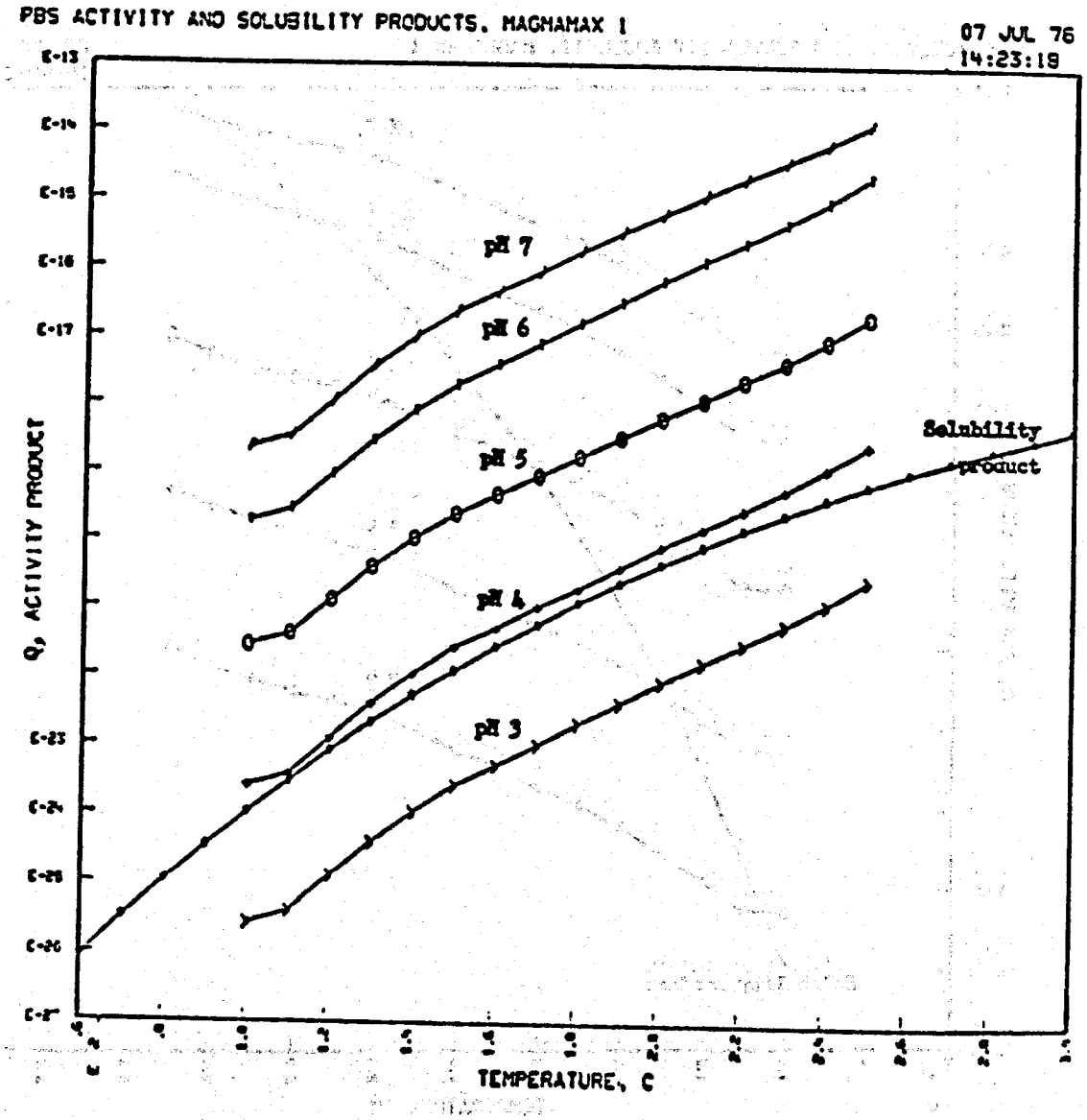

ZnS ACTIVITY PRODUCTS VS T, pH, AND Cl⁻
240°C
180°C
120°C
3.5
4.0
4.5
5.0
pH
-30
-29
-28
-27
-26
-25
-24
-23
-22
-21
-20
-19
-18
LOG Q
0 20 40 60 80 100 120
ppm Chloride/1000

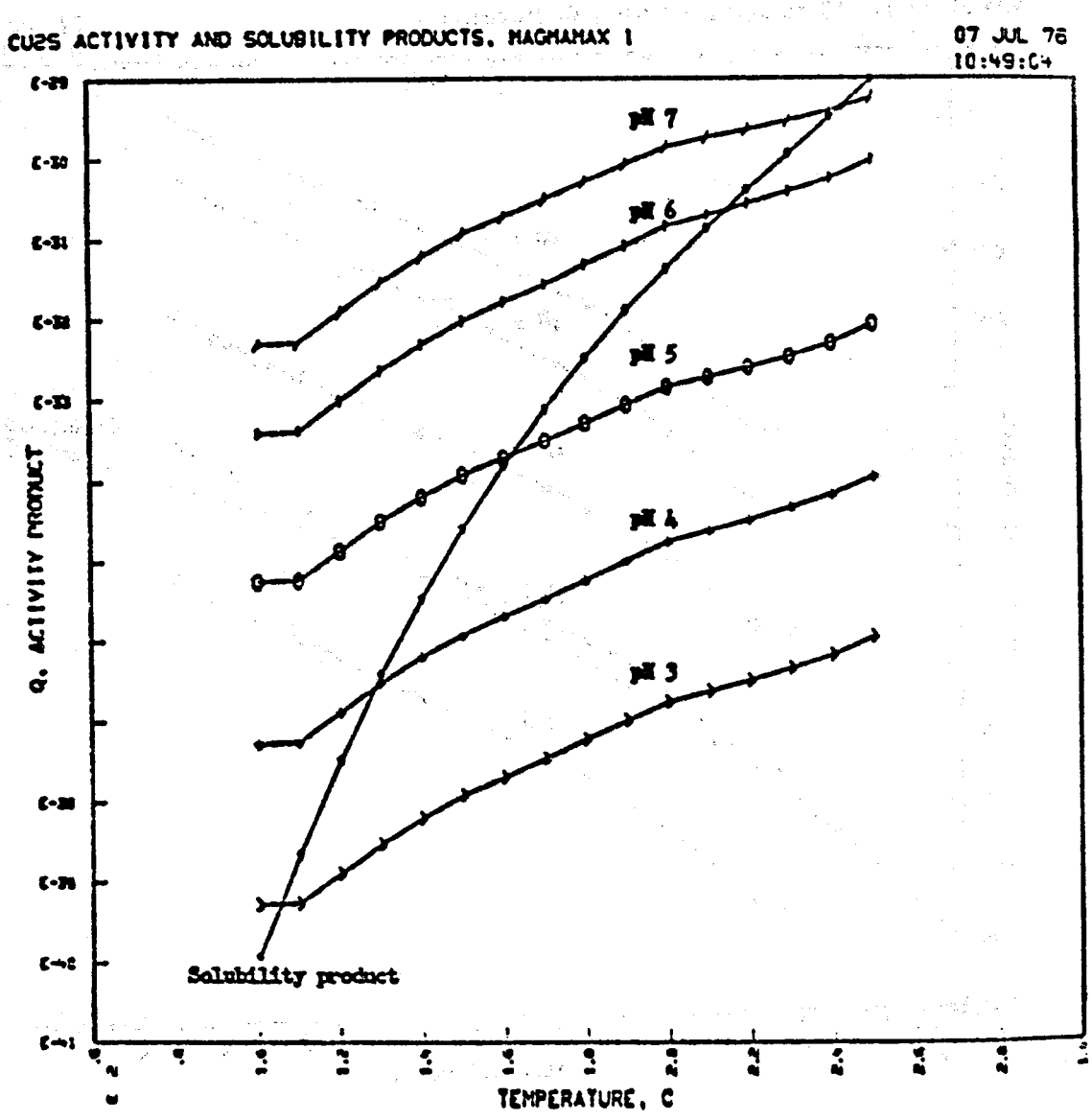

EXTRAPOLATED ACTIVITY COEFFICIENTS FOR Cu+
-4
-5
-6
-7
-8
log γ°
25 °C
50
100
150
200
250
300
NaCl MOLALITY
1
2
3
4
5
6
7
8

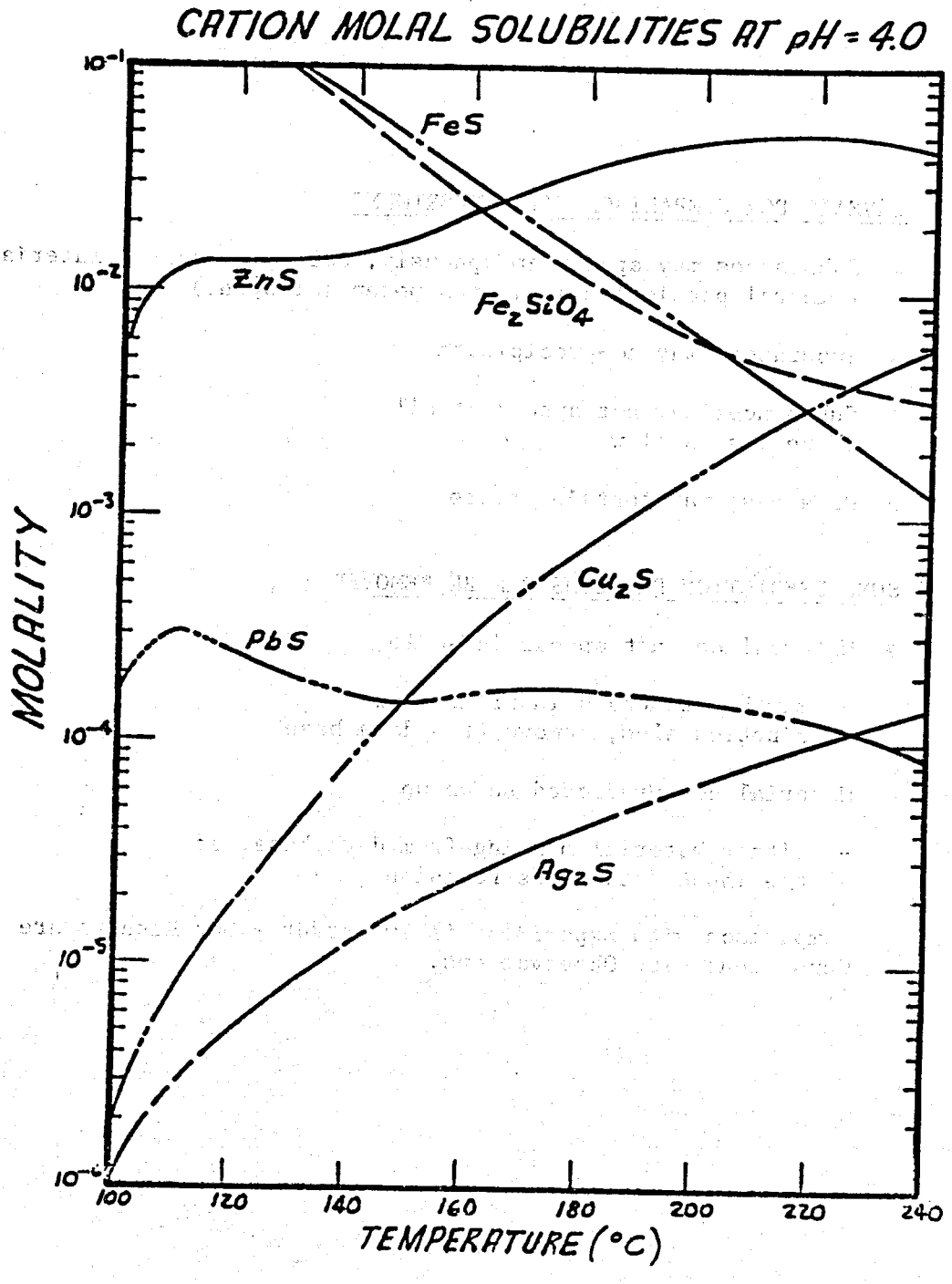

SULFUR DISTRIBUTION IN MAGMAMAX #1 FLUID
10^{-3}
10^{-4}
10^{-5}
H_2S PRESSURE, ATM
H_2S MOLALITY
HS^- pH 6.5
HS^- pH 6.0
HS^- pH 5.5
100
150
200
TEMPERATURE, °C


SIO2 ACTIVITY AND SOLUBILITY PRODUCTS, MAGMAMAX 1
07 JUL 76
15:47:23
Q, ACTIVITY PRODUCT
Solubility product
TEMPERATURE, C


CACO3 ACTIVITY AND SOLUBILITY PRODUCTS, MAGMAMAX I
26 JUL 76
15:12:49
pH 7
pH 6
pH 5
pH 4
pH 3
Solubility product
Q, ACTIVITY PRODUCT
TEMPERATURE, C


PBS ACTIVITY AND SOLUBILITY PRODUCTS, MAGMAMAX 1
07 JUL 76
14:23:18
pH 7
pH 6
pH 5
pH 4
pH 3
Solubility product
Q, ACTIVITY PRODUCT
TEMPERATURE, C


CUZS ACTIVITY AND SOLUBILITY PRODUCTS, MAGMAMAX 1
07 JUL 76
10:49:04
pH 7
pH 6
pH 5
pH 4
pH 3
Solubility product
Q, ACTIVITY PRODUCT
TEMPERATURE, C


CATION MOLAL SOLUBILITIES AT pH = 4.0
MOLALITY
TEMPERATURE (°C)
FeS
ZnS
Fe2SiO4
Cu2S
PbS
Ag2S
10-1
10-2
10-3
10-4
10-5
10-6
100
120
140
160
180
200
220
240

CAVEATS FOR COMPARISON WITH EXPERIMENT

- Substances may appear amorphously, not as predicted materials. (mineral prediction indicates potential pptn.)
- Substances may co-precipitate
- Substances may not appear at all (kinetics is slow)
- Data base may contain errors

SOME PREDICTION PROBLEMS CAN BE REMOVED

- Material doesn't appear in scale
  - may be suspended in brines; or
  - kinetics slow, remove from data base
- Material not predicted shows up
  - either material missing from data base; or
  - the input data needs revision

Comparison with Experiment is Important - Our Results are Consistent with Observations.

NEW GEOCHEMICAL CODE IS NEEDED

- Helgeson-Herrick now
  - designed for rock soln, not solids pptn
  - doesn't yield amounts or final concentrations
  - slow with large memory requirement
- New design should be
  - fast
  - small memory
  - suitable for subroutine in other codes
  - more versatile

FUTURE APPLICATIONS

- Scale problems
  - other temperatures
  - other additives
  - other wells
- Other uses
  - corrosion (Pourbaix diagrams)
  - reinjection equilibria