

NOTICE CONCERNING COPYRIGHT RESTRICTIONS

This document may contain copyrighted materials. These materials have been made available for use in research, teaching, and private study, but may not be used for any commercial purpose. Users may not otherwise copy, reproduce, retransmit, distribute, publish, commercially exploit or otherwise transfer any material.

The copyright law of the United States (Title 17, United States Code) governs the making of photocopies or other reproductions of copyrighted material.

Under certain conditions specified in the law, libraries and archives are authorized to furnish a photocopy or other reproduction. One of these specific conditions is that the photocopy or reproduction is not to be "used for any purpose other than private study, scholarship, or research." If a user makes a request for, or later uses, a photocopy or reproduction for purposes in excess of "fair use," that user may be liable for copyright infringement.

This institution reserves the right to refuse to accept a copying order if, in its judgment, fulfillment of the order would involve violation of copyright law.

HEAVY METAL SULFIDE SCALING IN A PRODUCTION WELL AT THE SALTON SEA GEOTHERMAL FIELD

D. L. Gallup⁽¹⁾ G. R. Andersen⁽¹⁾ and D. Holligan⁽²⁾

(1) Unocal Science and Technology Division, P. O. Box 76, Brea, CA 92621
(2) Unocal Geothermal Division, P. O. Box 7600, Los Angeles, CA 90051

ABSTRACT

Deposition of heavy metal sulfide scales in production wells and wellhead piping has been observed during the extraction of energy from the hypersaline, brine-dominated Salton Sea, California geothermal field. The primary constituents of these scales, which typically deposit at rates less than one centimeter per year, include galena (PbS), bornite (Cu_5FeS_4), sphalerite (ZnS) and troilite (FeS). These minerals precipitate as a result of 1) brine temperature reductions which decrease their solubility, and 2) the loss of CO_2 to the vapor phase during flashing which increases the pH of the brine. The metal sulfide scales form as hard, tenacious solids that are removed by periodic mechanical cleaning. An example of a scale deposition episode for a well in the field is provided to illustrate the propensity for precipitation of the metal sulfides from the brine.

INTRODUCTION

Scale deposition is recognized as an important problem hindering commercial utilization of geothermal energy from high temperature, hypersaline brines. The deleterious effects of silica and calcium carbonate precipitation in geothermal wells and surface equipment have been well-documented (1,2). A less common class of scale that precipitates from certain brines is the heavy metal sulfides. The formation of copper and iron-rich sulfide scales from wells producing saline brine was first described by Skinner, et al, (3) at the Salton Sea geothermal field. These sulfide minerals were later found to be intermixed with silicate scales in test facilities constructed at the field (4). Metal sulfide scale deposition has also been observed in low temperature geothermal fields in the Paris basin (5) and a high temperature field on the island of Milos in Greece (6).

Upon exploitation of the Salton Sea geothermal field by Union Oil Company of California in the early 1980s, metal sulfide scaling was observed in production wellbores. Wells producing brine to a 10 MWe steam gathering system demonstration facility slowly scaled with a hard, tenacious, heterogeneous metal sulfide deposit in the wellbore

and wellhead piping. Scaling rates in these wells were generally less than 1 cm per year.

Throughout the flow testing phase of production wells in the southern portion of the Salton Sea field, numerous sulfide scale deposits were retrieved from wellhead piping and production strings. The composition of the scales varied from well to well as did the brines from which they precipitated. In general, the primary constituents of the scales were the minerals, galena (PbS), sphalerite (ZnS) and troilite (FeS), present in coarse-grained, highly crystalline intergrowths. Occasionally, alumino-silicate formation minerals, quartz and iron silicate were interspersed with the bulk sulfide minerals.

SULFIDE SCALE DEPOSITION - AN EXAMPLE

For illustration, an example of metal sulfide deposition from a producing well in the Salton Sea field is provided. Table 1 shows the composition of the brine from which the scale precipitated. The brine is comprised primarily of sodium, potassium and calcium chlorides. Heavy metals including lead, copper, iron and zinc are present in minor quantities in the brine. Carbon dioxide is the major dissolved gas in the brine; hydrogen sulfide is a minor gas component.

Table 2 presents the conditions of a brine production episode for the example well which resulted in the deposition of a significant quantity of heavy metal sulfide scale. This well was produced for 256 days at an average flow rate of 133,600 kg per hour. Scale, ranging in thickness from 0.04 to 0.18 cm, was deposited on a production string (22 cm in diameter and 378 m in length). The scale was thickest at the top of the liner and tapered gradually to the bottom. During production, the brine was allowed to flash in the wellbore resulting in a pressure drop of about 800 kPa and a temperature drop of about 25°C.

Scales from several depths of the retrievable production string were analyzed by x-ray diffraction and emission spectrometric methods. The results of these analyses are provided in Table 3. Also included in Table 3 are calculated mineralogical compositions of the scales employing the quantitative elemental analytical data. The bulk chemistries and calculated mineralogies of the

scale samples are entirely consistent with the results of the x-ray diffraction studies. In this particular well, galena is the predominant metal sulfide deposited as scale. Lesser amounts of sphalerite, troilite and bornite comprise the remainder of the metal sulfide deposits. Also present in the scales is an amorphous ferric silicate (7). The metal sulfide deposits are coarsely crystalline exhibiting cubic terminations on the brine-side face, and form a continuous layer on the inside of the liner.

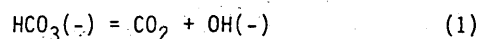
From the scale composition data and estimates of the weight of scale deposited on the production string, we have attempted to obtain a scale material balance. It is estimated that 2 parts per million (ppm) of material in solution was deposited as scale on the retrievable production string during this particular production episode. The scale consists of about 1 ppm lead, 0.2 ppm zinc, 0.4 ppm iron and 0.2 ppm sulfur. That lead, followed by iron and zinc, is the order of total metal deposited in the wellbore, correlates with the solubility products of these metal sulfides. As shown in Figure 1 (8), at 250°C and 3 molal sodium chloride solution, solubility products of FeS and ZnS are nearly the same, but are significantly greater than PbS. Thus, zinc and iron sulfides are expected to be more soluble in Salton Sea brine than lead sulfide. While this appears to be true for the bulk scale, it is interesting to note that ZnS and FeS predominate the scale deposited at the bottom of the liner and PbS predominates at the top. We recognize that any differences in precipitation sequence can result from mass action (more iron and zinc are present in the brine than lead), from kinetically-controlled reactions and the formation of various complexes in solution that stabilize the metals with respect to precipitation.

Scanning electron microscopy and electron microprobe studies of the deposits (Figures 2 and 3, respectively) show that dendritic crystalline growth is important in the precipitation process. This growth mechanism is characteristic of diffusion-limited supersaturation conditions that may exist in hypersaline brines. In the case of these sulfide scales, dendritic growth likely occurs by diffusion of solvated metal ions to the growing crystal surface followed by deposition of the ions and release of water molecules away from the growing surface. These studies further show that post-precipitation is important in the scaling mechanism. Post-precipitation involves the formation of a second insoluble substance on a precipitate that has already formed, as a result of differences in rates of precipitation. Sphalerite, in particular, shows a definite tendency to post-precipitate on the other metal sulfides. Crystals of galena and troilite induce the post-precipitation of sphalerite as hydrogen sulfide is adsorbed on the solid sulfide as bisulfide or sulfide ion, owing to the strong attraction of the metal sulfide lattice for these ions (9). An example of the sequential post-precipitation of sphalerite on galena is shown in Figure 3.

SCALE DEPOSITION CHEMISTRY

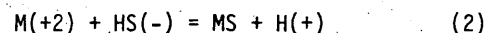
It is well-understood that the deposition of metal sulfides from geothermal brine is induced by reductions in temperature and the exsolution of acidic gases during vapor flashing (10). When carbon dioxide partitions to the vapor phase during flashing, the pH of the brine increases significantly.

At the Salton Sea field, we have estimated that the pH of the brine in transit up the example production string increases from about 5.0 to 5.1 (over a distance of 378 meters), and the brine temperature decreases from about 260°C to about 230°C. The increase in pH is due to release of primarily CO₂ described by Reaction 1:



A similar reaction involving hydrogen sulfide release from bisulfide ion also occurs during flashing.

In the Salton Sea geothermal reservoir (pH=5.0, 260°C), sulfide in brine is probably present primarily as bisulfide ion, HS(-). During production of the brine to the surface, some H₂S is released to the vapor phase. However, sufficient bisulfide remains for very fast reaction with the heavy metals to deposit scale:



where M is Cu, Fe, Pb and Zn. As the pH of the brine increases slightly across the production string via CO₂ release, Reaction 2 is driven to the right resulting in ubiquitous sulfide scale deposition.

METAL SULFIDE SOLUBILITY AS A FUNCTION OF TEMPERATURE AND pH

The effect of pH on the solubility of metal sulfides at ambient temperature has been studied in detail (11, 12). Galena has been shown to be more insoluble than sphalerite and troilite over the pH range, 3 - 11. Metal sulfide solubilities have also recently been studied in concentrated sodium chloride solutions to 300°C (13). To improve our understanding of the effect of both pH and temperature on the solubility of sulfides in hypersaline geothermal brines, laboratory autoclave studies were performed. Synthetic brines consisting of 4.3 molal sodium chloride solution were spiked with lead chloride. After appropriate pH adjustment with hydrochloric acid (4.0-5.5), the brine was placed into a one liter Hastelloy C-276 autoclave (Autoclave Engineers). The autoclave was then purged with pre-purified nitrogen to preclude oxygen. Hydrogen sulfide gas (15 ppm in the gas phase) was charged into the autoclave and the mixture was heated with stirring. The concentration of H₂S charged into the autoclave (0.0006 m) was sufficient to precipitate all of the lead in the brine (0.0003 m). Upon heating to the desired temperature, a 10

mL aliquot was retrieved through a sample port and immediately filtered through a 0.22 micron Millipore filter. The filtrate was analyzed for lead by ICP spectrometric techniques. No attempts were made to analyze the pH or H_2S concentration in the brine aliquot.

Table 4 and Figure 4 present the results of the analyses of the autoclave study. The solubility of lead sulfide was monitored by determining the concentration of lead in the heated sample and comparing with the metal values initially present in the brine prior to heating in the presence of H_2S . The ratios of the lead in solution (Pb) to the initial concentration (Pbo) are employed to determine the effect of pH and temperature on the solubility of galena in the synthetic brine to 260°C. As expected, the metal sulfide solubility increases with temperature and lower pH of the brine established before reaction with H_2S . The solubility of galena in the synthetic brine is significantly greater than that reported in pure water due to chloride complexing (14). The results of the study are similar to those reported in sodium chloride solutions (8, 13). In the synthetic brine solution, lead is apparently in the form of lead chloro-complexes, although heavy metals have been postulated to be transported in geothermal brines via thio-complexes especially below 150°C (15).

Barrett and Anderson (13) have calculated the solubility of galena and sphalerite in Salton Sea geothermal brines. For brine exhibiting a temperature of 300°C, chloride concentration of 5.9 molal, pH of 5.4 and H_2S concentration of 0.00064 molal, the solubility of sphalerite is -3.17 (expressed as log m) and the solubility of galena is -4.36. This compares with reported measured values of -1.9 and -3.3, respectively. The calculations were made at high temperature from extrapolations of experiments conducted below 100°C. These calculations compare with our experimentally-determined galena solubility of -3.6 at 260°C, 4.3 m NaCl, pH 5.0 and 0.0005 m H_2S initially charged into the autoclave. This measured solubility is also very similar to that calculated by McKibben and Elders (16) for Salton Sea geothermal brine (~2.9).

The experimental data in Table 4 predicts that production to the wellhead of pH 5.0 hypersaline brine from the Salton Sea reservoir (~260°C) at the example well location, resulting in a slight pH increase (0.5 units) and a decrease in temperature to about 230°C will result in a Pb/Pbo difference of about 0.04 (0.90 vs 0.86, extrapolated). This difference corresponds to the loss of about 2 ppm lead from solution. This compares reasonably well with our material balance calculation for the example well of deposition of 1 ppm lead from the brine in the retrievable liner. That heavy metal scales are deposited in the example well is evidence for supersaturation of the mineral species in the geothermal brine.

METAL SULFIDE SCALE INHIBITION

Heavy metal sulfide scaling rates at the Salton Sea geothermal field are sufficiently low that no special deposition inhibition technique is required. Generally, wells are cleaned of sulfide scale deposits by mechanical drillout. However, we have investigated methods to inhibit the deposition of these scales in production wells and surface equipment. Several potential methods to inhibit heavy metal sulfide scaling from geothermal brines have been proposed (17). These methods include decreasing the brine pH by acid addition, increasing the brine oxygen fugacity, adding oxidizing agents to the brine and treating brine with commercially-available scale inhibitors.

Our autoclave studies discussed above suggest that decreasing the brine pH by 0.1 to 0.3 units will control sulfide scale deposition in the production string. Based on data presented in Table 4, it appears that lowering the brine pH just below 5.0 is expected to inhibit galena precipitation during production of brine in the example well when flashing and temperature reduction occur. The injection of acid into the brine will drive Reaction 2 to the left to maintain the heavy metals in solution. A process for acidifying brine to control metal sulfide and iron silicate scaling has been developed (18). An alternative method to modify the brine pH by injection of carbon dioxide has also been described (19).

Injecting air or chemical oxidizing agents into brine to oxidize H_2S to by-products that will not precipitate heavy metals has proven useful (20). Special precaution must be taken in this process to mitigate corrosion and to avoid precipitating such species as barite, calcium sulfite, sulfur and ferric silicate, however.

Injection of commercially-available inhibitors to control downhole calcite and metal sulfide scales has been recently demonstrated (21, 22). The most common inhibitors employed in these geothermal applications are those which act in the threshold or crystal growth blocking modes. The inhibitors have controlled calcite scaling at high temperature and metal sulfide scaling at low temperature only. Whether these inhibitors including dispersants, phosphonates, carboxylic acids, amines, and amides can control metal sulfide scaling in hypersaline geothermal brines at high temperatures, to our knowledge, has yet to be demonstrated. Downhole inhibitor delivery systems including annular and coiled tubing have been described (23).

CONCLUSION

Heavy metal sulfide scale deposition in production wells and surface equipment has been observed during extraction of energy from the Salton Sea, California geothermal field. Sulfide scaling in wellbores is generally a slow process, but scale build up can eventually deleteriously

curtail steam production. Mixed-metal sulfides deposited in wells can be mechanically removed from retrievable production strings during remedial workovers. Methods have been developed to inhibit sulfide scaling at the field. Laboratory studies on galena solubility in synthetic brine have assisted in understanding the effect of pH on scale deposition. Further research is required to identify sulfide-specific inhibitors that can function in high temperature hypersaline environments and to improve downhole inhibitor delivery systems.

ACKNOWLEDGMENT

We thank Unocal Corporation management for permission to publish these results.

REFERENCES

1. Wahl, E. F., Geothermal Energy Utilization, John Wiley and Sons, New York (1977).
2. Ellis, A. J. and Mahon, W. A. J., Chemistry and Geothermal Systems, Academic Press, New York (1977).
3. Skinner, B. J., et al., Econ. Geol. (1967) 62, 316.
4. Austin, A. L., et al., Lawrence Livermore Laboratory Geothermal Energy Program Status Report Jan. 1976 - Jan. 1977, UCRL - 50046 - 76 (Apr. 1977).
5. Criaud, A. and Fouillac, C., Geothermics, (1989) 18, 73.
6. Karabelas, A. J., et al., Geothermics (1989) 18, 169.
7. Gallup, D. L., Geothermics (1989) 18, 97.
8. Helgeson, H. C., Am. J. Sci. (1969) 267, 729.
9. Kolthoff, I. M. and Griffith, F. S., J. Phys. Chem., (1938) 42, 531.
10. Kindle, C. H., et al., Battelle Pacific Northwest Laboratories Report - 4767 (Sept. 1984).
11. US EPA, Summary Report - 625/8-30-003 (1980).
12. Bartlett, R. W., et al., US Bureau of Mines, PYU 7937 (Dec. 1979).
13. Barrett, T. J. and Anderson, G. M., Geochim. Cosmochim. Acta, (1988) 52, 813.
14. Nriagu, J. O., Am. J. Sci., (1971) 271, 157.
15. Kaz'min, L. A. and Karpov, I. K., Aka. Nauk SSSR, Sibersk Otd. Inst. Geokhim. Ezh. Irk. (1972) 319.
16. McKibben, M. A. and Elders, W. A., Econ. Geol. (1985) 80, 539.
17. Jackson, D. D. and Hill, J. H., Lawrence Livermore Laboratory Report - UCRL - 51977 (Jan. 1976).
18. Jost, J. W. and Gallup, D. L., US Patent 4,500,434 (1985).
19. Kuwada, J. T., Geotherm. Res. Council Bull., (1982) 11, 3.
20. Jost, J. W., US Patent 4,224,151 (1980).
21. Corsi, R., et al., Geotherm. Res. Council, Trans., (1985) 9, 239.
22. Honegger, J. L., et al., Geothermics, (1989) 18, 137.
23. Pieri, S., et al., Geothermics, (1989) 18, 249.

Table 1. Wellhead Brine Composition (pH = 5.5)

Analyte	ppm	Analyte	ppm	Analyte	ppm
As	1	Li	120	Sr	330
Ba	70	Mg	90	Zn	250
B	222	Mn	650	Cl	122,000 (m Cl=4.3)
Ca	20,200	Na	43,200	CO ₂	6,200
Cu	2	Pb	50	H ₂ S	16
Fe	320	Rb	50	NH ₃	350
K	10,600	SiO ₂	405	TDS	192,000

Table 2. Well Production History

Production Duration	6,144 hours
Total Mass Flow	821,000,000 kg
Average Mass Flow	133,600 kg/hr
Average Wellhead Temperature	225°C
Average Wellhead Pressure	2,480 kPa
Production Liner (diameter)	22 cm
(length)	378 m
Scale Thickness (top)	0.18 cm
(bottom)	0.04 cm

Table 3. Scale Analyses

X-Ray Diffraction:

Sample	Depth, m	Major (>20%)	Moderate (5-20%)	Minor (<5%)
1	0	PbS	Amorphous	---
2	12	PbS	---	Fe ₃ O ₄ , FeS
3	378	Fe-rich ZnS	Fe ₃ O ₄	Cu ₅ FeS ₄ , PbS

Quantitative Analysis (wt%):

Sample	Ag	Cu	Fe	Pb	S	Si	Zn
1	0.1	0.1	4.9	54.4	8.5	4.8	1.0
2	0.1	0.1	9.5	55.8	10.1	3.0	1.0
3	0.1	0.4	37.9	6.1	14.6	4.2	13.7

Calculated Mineral Modes (wt%):

Sample	Ag	Cu ₅ FeS ₄	Fe(OH) ₃ *SiO ₂	Fe ₃ O ₄	FeS	PbS	ZnS	Total
1	0.1	0.2	28.5	---	1.7	62.6	1.5	94.6
2	0.1	0.2	17.8	2.6	2.7	64.2	1.5	89.1
3	0.1	0.6	25.0	24.0	19.2	7.0	20.1	96.0

Table 4. Lead Sulfide Solubility in Synthetic Geothermal Brine

T, °C	Pb/Pb ₀			
	pH = 4.0	pH = 4.5	pH = 5.0	pH = 5.5
25	0.06	0.06	0.08	0.01
75	0.29	0.22	0.18	0.10
100	0.36	0.35	0.28	0.12
150	0.81	0.70	0.59	0.42
200	0.91	0.85	0.79	0.60
230	0.99	0.93	0.89	0.74
260	0.99	0.94	0.90	0.78

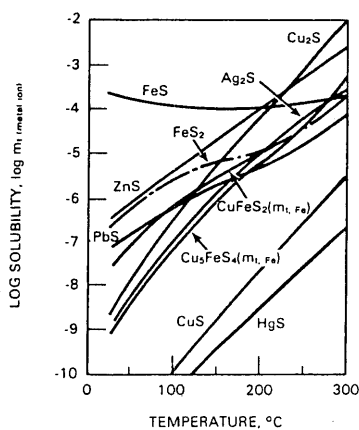
4.3 m NaCl, 0.0003m Pb₀, 0.0006 m H₂S₀

Figure 1
METAL SULFIDE SOLUBILITIES
IN 3m NaCl (Ref. 8)

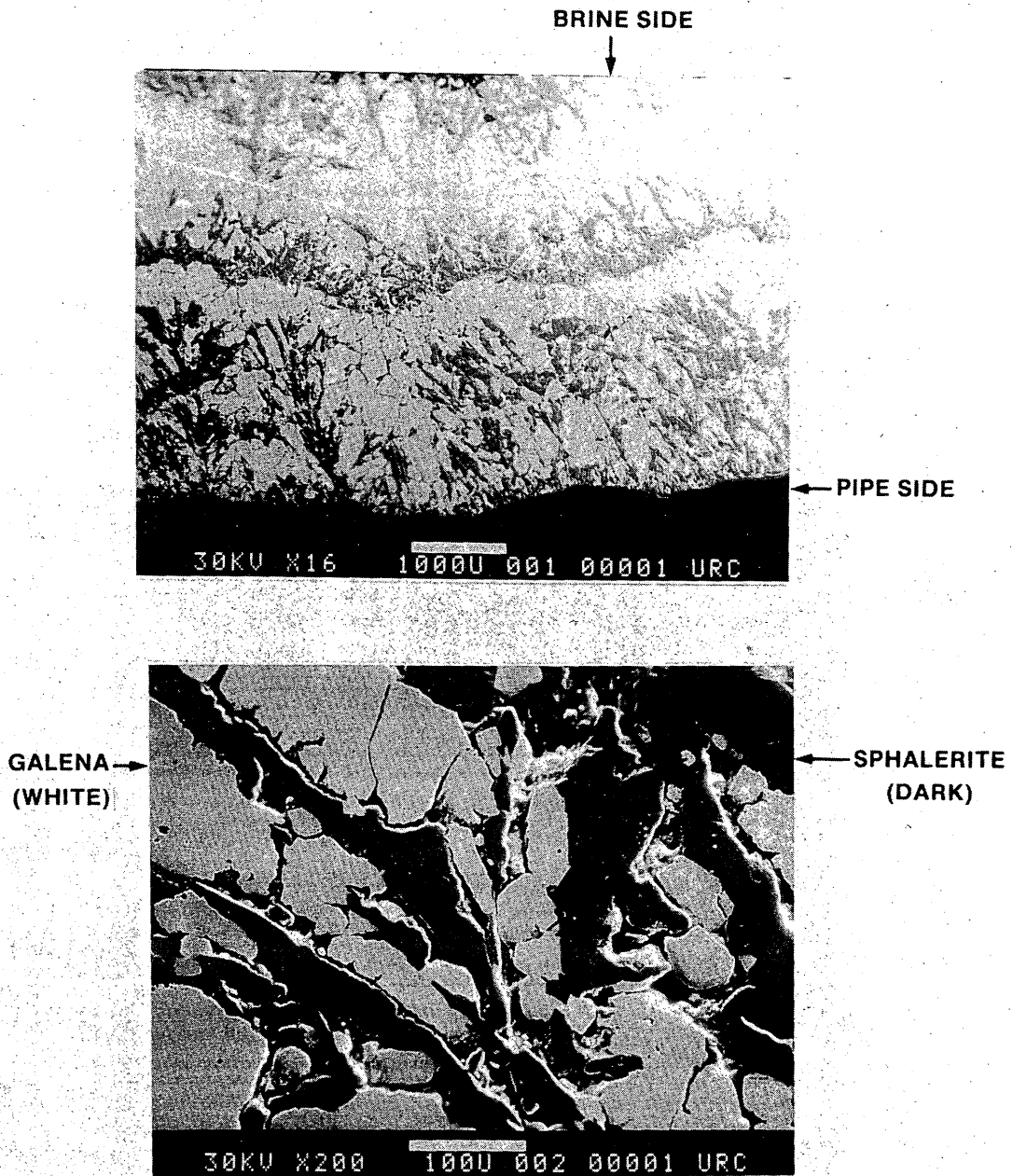


Figure 2
SCANNING ELECTRON MICROGRAPH
METAL SULFIDE SCALE

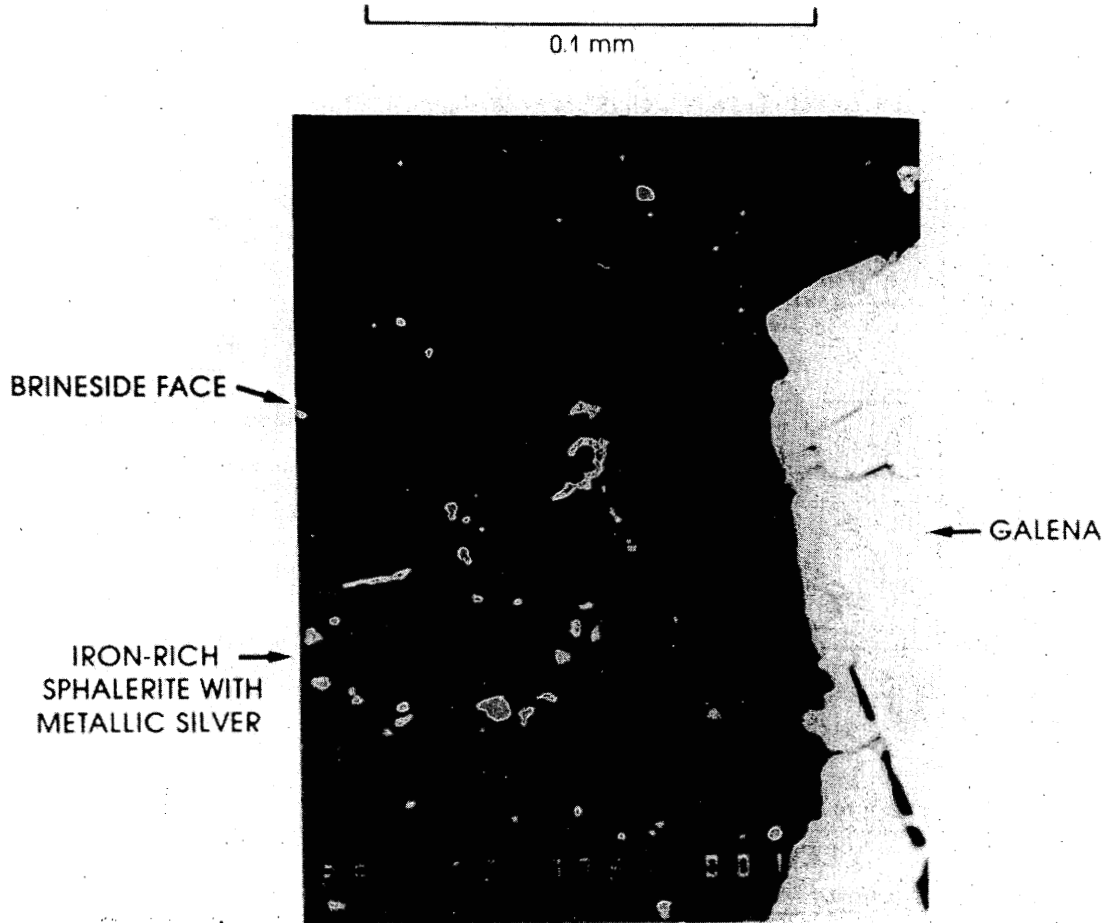


Figure 3
ELECTRON MICROPROBE
METAL SULFIDE SCALE

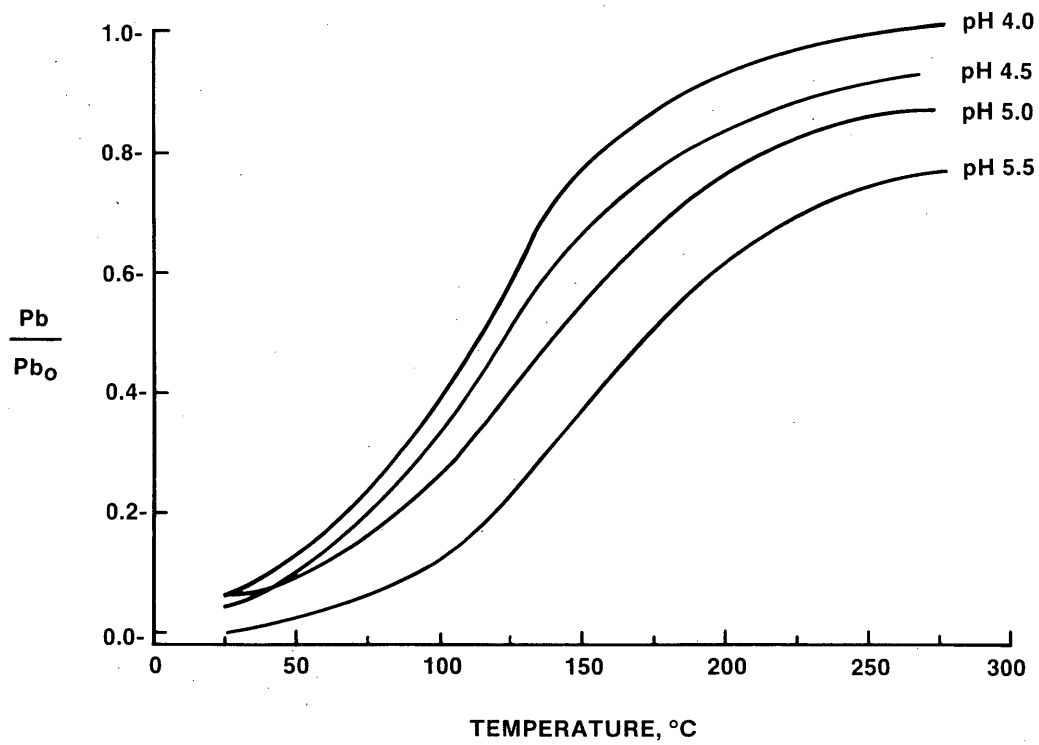


Figure 4
LEAD SOLUBILITY IN SYNTHETIC BRINE
IN THE PRESENCE OF H₂S