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SCALE CONTROL STUDIES AT THE CERRO PRIETO GEOTHERMAL PLANT

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ABSTRACT

The high silica contents (over 900 mg/l) of the Cerro Prieto geothermal brines cause various scaling problems at the electric power facility. The scaling tendency of the brine is a direct function of the silica saturation ratio. A scaling rate of 1-10 mm/yr was experienced at low saturation ratios ($S_R \leq 2$); 100-400 mm/yr at S_R higher than 3. Pilot plant tests satisfactorily predict scaling rates in commercial equipment. Amorphous silica deposited in process equipment can be dissolved by NaOH, KOH, and NH_4HF_2 . The use of chemical products to remove scale from well pipes can be a better method of scale control. A process for colloidal silica removal has been developed using 20-30 ppm of lime as a flocculant agent.

INTRODUCTION

The Mexican electricity authority, Comisión Federal de Electricidad (CFE), started the exploitation of the Cerro Prieto geothermal field in 1973 by means of two 37.5 MW units. At the beginning of 1979 two additional 37.5 MW units were installed. And, at the end of 1981 it started running the fifth unit, a 30 MW unit, that produces electricity from the other four units' disposal brine. These five units make up the Cerro Prieto I Power Plant (CP-I), with a total capacity of 180 MW. Because the Cerro Prieto brine is high in silica composition (>900 mg/l) a number of scaling studies were conducted to select the flash separator pressures.

In 1984, a more advanced type of Power Plant, Cerro Prieto II (CP-II) with two 110 MWe units began producing electricity. And finally, at the end of 1985, the Cerro Prieto III Power Plant (CP-III) was completed. In these cases a number of scaling studies were also practiced in order to select the minimum pressure in the last flash separators.

Currently, preliminary engineering studies are being made for the installation of the Cerro Prieto IV Power Plant (CP-IV). As this plant might be located in a farming area, reinjection is one of the best alternatives for disposal of the brine. Part of the preliminary engineering studies are the scaling and brine treatment studies.

Since 1977, IIE has carried out a number of scaling studies at the Cerro Prieto geothermal field beginning with the fifth unit flash evaporation station project. For the time being new scaling studies are under development. This paper summarizes the most important results obtained during the last ten years and describes the program to be developed in the near future.

OBJECTIVE OF SCALING STUDIES

The scaling studies practiced at Cerro Prieto have had different specific objectives (Mercado, et al. 1981). Nevertheless, the overall objectives are: (1) To improve the energy recovery efficiencies from the extracted geothermal fluid, and (2) To minimize the power plant operation and maintenance costs.

CHEMISTRY OF THE BRINE

Chemical Composition of the Brine

Table 1 shows the chemical composition of the brine of some wells from CP-I, CP-II, and CP-III areas that were under commercial exploitation at the time the samples were taken. The data from table 1 indicate that Cerro Prieto brine is of an alkali chloride water type.

Origin of the Brine

The Cerro Prieto brine was originated from a mixture of sea water and Colorado River water (Truesdell et al., 1981). These studies have shown that

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Table 1. Chemical composition (mg/l) of separated brine (P= 0 psig) at Cerro Prieto geothermal field.

WELL	DATE	pH	Na	K	Li	Ca	Cl	HCO ₃	SiO ₂	TDS
<u>CERRO PRIETO I</u>										
M-14	9/17/80	8.0	5938	1103	14	319	10770	115	832	17096
M-19A	9/17/80	7.4	8193	1867	20	451	15184	77	1123	26971
M-21A	9/17/80	7.2	5973	1233	14	394	11151	103	961	19492
M-91	4/27/84	7.1	10021	2704	27	373	18547	71	1308	34003
E-4	4/24/84	6.6	10972	3066	29	414	20299	49	1002	36435
E-7	4/25/84	7.0	12319	3449	33	489	23274	47	1266	41624
<u>CERRO PRIETO II</u>										
M-169	4/26/84	7.1	11552	3164	29	491	21462	57	1266	39725
T-348	11/29/83	6.1	10830	3076	30	422	21655	7	1161	40650
T-400	3/12/86	7.2	11493	3249	33	533	21963	28	1257	42189
<u>CERRO PRIETO III</u>										
M-110	10/19/81	7.7	7580	1914	26	366	15620	57	1093	27195
M-120	4/26/84	6.7	10151	2946	30	382	18815	51	1112	33762

the concentrations of chloride, bromide and deuterium originated from a mixture of oceanic brine and river water were unaltered during passage through the geothermal system. These constituents of the fluid are not contained in normal rocks and cannot normally be taken up or released during rock reactions. Preliminary thermodynamic calculations have been done (Truesdell et al., 1982) in order to establish the state of the fluid with respect to certain reactions and attempt to determine what reactions control the composition of the fluid. The calculations have shown that apparently the hydrothermal fluid is in chemical equilibrium with the minerals in the aquifer such as K-feldspar, Na-feldspar, high Na-plagioclase, calcite, anhydrite, pyrite, pyrrhotite, graphite (coal) and possibly magnetite.

Changes in Silica Concentration

By extrapolation of chemical data, it is possible to state that Cerro Prieto brine reaches the solubility equilibrium with respect to quartz at reservoir conditions. This equilibrium is disturbed when the geothermal fluid is extracted, due mainly to the drop of temperature caused by the flashing process. In addition, the separation of steam decreases the liquid volume causing an increase in the concentration of all the chemical species. At the beginning of the flash process the brine becomes supersaturated with respect to quartz.

Nevertheless, when the changes in temperature are big enough the brine becomes highly supersaturated with respect to amorphous silica. Figure 1 shows the changes in silica concentration during the flashing of the brine from reservoir to atmospheric conditions for the range of silica composition of the Cerro Prieto brines.

Silica Polymerization

Monosilicic acid, Si(OH)₄ is the form of dissolved silica (quartz) in the Cerro

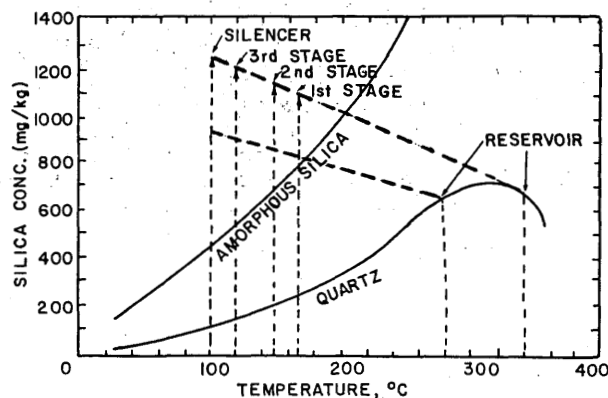


Figure 1. Trajectories for the brine silica concentration as a function of steam separation temperature at Cerro Prieto.

Prieto brines (also known as monomeric silica). When the brine is supersaturated with respect to amorphous silica, the monomer polymerizes to colloidal particles that nucleate in the brine. The rate of silica polymerization process in the Cerro Prieto brine depends very strongly upon the silica saturation ratio. In general polymerization is very slow when the saturation ratio is below two, and very fast when the saturation ratio is above three (Weres et al., 1980). Figures 2 and 3 show the silica polymerization rates of the brines from wells M-14, M-19A, and M-25. High silica polymerization rates causes serious problems of precipitation and deposition of silica on the surfaces in contact with the brine.

SCALING RATE MEASUREMENTS

Pilot Plant Test

In order to select the minimum pressure in the last stage of flashing, scaling tests were performed using pilot equipment designed to determine the scaling tendency of the brine to deposit minerals as a function of the pressure or temperature and the number of steps of steam separation (Mercado, et al. 1979). Figures 4 and 5 are schematic diagrams of the pilot equipment tested showing the sites where scaling rates were measured. Figure 6 shows scaling rate as a function of steam separation pressure for one step of separation using brine from well M-21A in a pilot equipment like that shown in Figure 4, handling 20,000 lb/h of brine. Scaling rates as a function of silica

concentration in the brine are shown in Figure 7, for several Cerro Prieto wells. Well M-53 is located in the Cerro Prieto III area, and the other wells located in the Cerro Prieto I area.

Commercial Equipment

Deposition of solids in the turbines were experienced during the first years of operation of the Cerro Prieto I power plant. Minor changes in the mechanical design of steam separators considerably reduced the amount of liquid drops carried by the steam stream, solving the problem of deposits in the turbines.

Minor scaling problems were experienced in the handling of disposal brine during the first six years of operation at Cerro Prieto I power plant. This was due mainly to the high temperature of the brine (170 °C) and its corresponding low level of silica oversaturation. Figure 8 shows the maximum scaling rates experienced in the disposal brine pipes from units 1 to 4 at the Cerro Prieto I power plant.

CHARACTERIZATION OF SCALES

Production Wells

X-ray diffraction studies (Hurtado, et al, 1984) were conducted in order to identify the minerals that were deposited on the production line of nine different wells. In order to determine the relative abundance of the minerals, complementary atomic absorption and conventional wet chemistry analysis were also practiced on

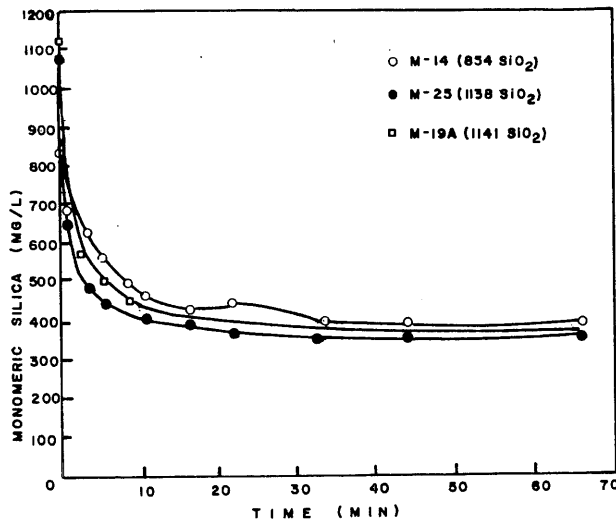


Figure 2. Rates of silica polymerization from separated brine of wells M14, M19A, and M-25. T= 95 °C.

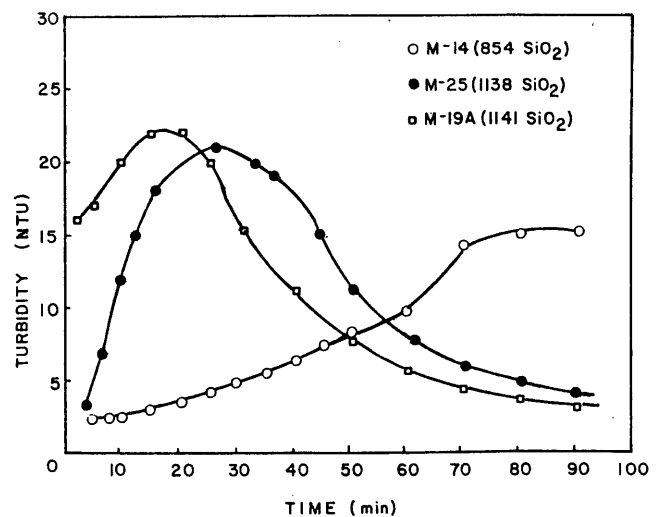


Figure 3. Turbidity vs. time from separated water of wells M14, M19A, and M-25. T=95 °C.

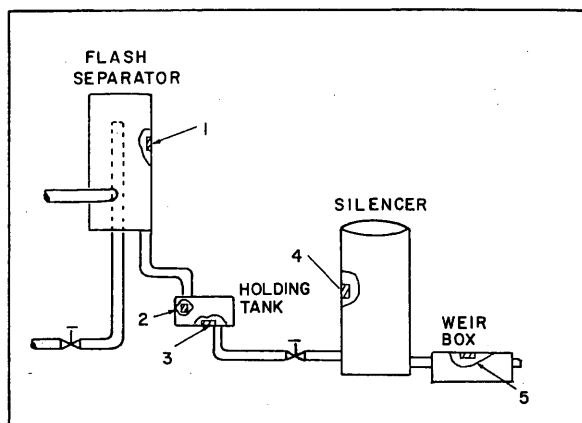


Figure 4. Pilot scale test facility for measurement of scaling rate using one stage of steam separation.

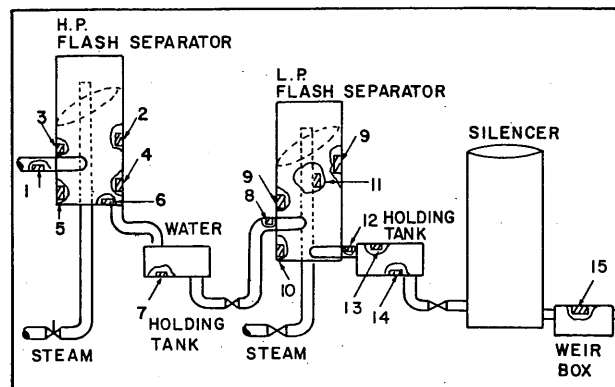


Figure 5. Pilot scale test facility for measurement of scaling rate using two stages of steam separation.

the same set of samples. The results from X-ray analysis are summarized in Table 2. A high proportion of amorphous silica compounds caused some interferences in the diffraction spectra. More than fifteen minerals were identified from about ninety samples of scale deposited on the production pipe of nine different wells. The main minerals deposited were amorphous silica compounds, sphalerite, galena, calcite, and luzonite.

Process Equipment

Amorphous silica was the main compound deposited in the process equipment. Minor proportion of iron sulfides and oxides were present. In general silica concentration in the solids deposits was over 90 %, weight.

Figures 9 and 10 show the typical morphology of colloidal amorphous silica deposited by an homogeneous nucleation process. In some cases, when the saturation rate was low, vitreous silica deposits were experienced (Figs. 9 and 10).

SCALE CONTROL TESTS

Acidification

It is well known that the reaction of silica polymerization can be quenched by modification of pH. This fact represents a potential method for the control of silica deposition. In order to test the concept, laboratory and pilot plant tests

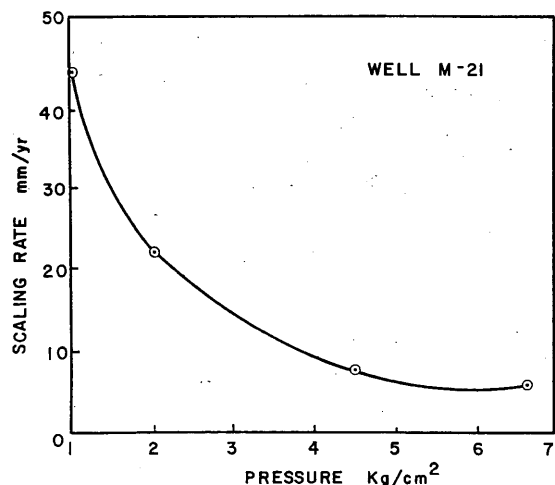


Figure 6. Scaling rates vs. steam separation pressure from M-21A brine.

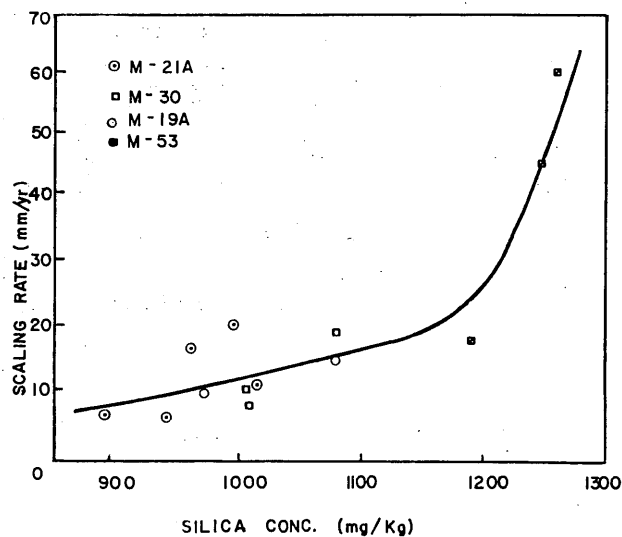


Figure 7. Scaling rates vs. silica concentration in the brine.

Table 2. Minerals identified in the scale deposits at the production pipes.

Mineral	M-7	M-8	M-11	M-21A	M-26	M-53	M-102	M-103	M-181
Amorphous		X	X			XXX	X	XXX	XXX
Anhydrite				X					
Anglesite								X	
Calcite	XXX	XX		X	XXX				T
Cubanite									
Chalcopyrite							T		
Galena		T	x	X		X	X	XX	T
Germanite				X					
Gypsum		T							
Halite									
Luzonite		T	x				X	X	T
Magnesioferrite						X			T
Montmorillonite			x						
Magnetite			T				X		
Pyrrhotite									
Quartz	x	T			T	T			
Sphalerite		T	x	X		X	X	X	T
Sylvite									
Talc			x						X
Vermiculite				X					X

XXX= Most abundant; X= Important proportion; x= Low proportion; T= Traces.

Table 3. Condensed formula of deposited minerals.

Mineral	Formula
Anhydrite	CaSO ₄
Anglesite	PbSO ₄
Calcite	CaCO ₃
Chalcopyrite	CuFeS ₂
Galena	PbS
Gypsum	CaSO ₄ .2H ₂ O
Halite	NaCl
Luzonite	Cu ₃ AsS ₄
Magnesioferrite	MgFe ₂ O ₄
Montmorillonite	(Na,Ca) _{0.33} (Al,Mg) ₂ Si ₄ O ₁₀ (OH) ₂ .nH ₂ O
Magnetite	Fe ₃ O ₄
Pyrrhotite	FeS
Quartz	SiO ₂
Sphalerite	ZnS
Sylvite	KCl
Talc	Mg ₃ Si ₄ O ₁₀ (OH) ₂
Vermiculite	(Mg,Ca) _{0.9} (Mg,Fe) ₃ (Si,Al) ₄ O ₁₀ (OH) ₂ .5H ₂ O

were performed. Figure 11 shows the results obtained in a pilot plant test using this scale control method. The basic data from the mentioned test were as follows,

Well No: M-53
 Brine pressure: 20-40 psig
 Flow rate: 4,000 lb/h
 Period of time: 40 h
 Silica conc.: 1,352 ppm

Figure 11 indicates that the injection of hydrochloric acid at pH 5.0 reduces the scaling rate of the brine from 461 mm/yr to 21 mm/yr, this is a factor of 20, or one order of magnitude. The tests conducted did not include measurement of corrosion rates.

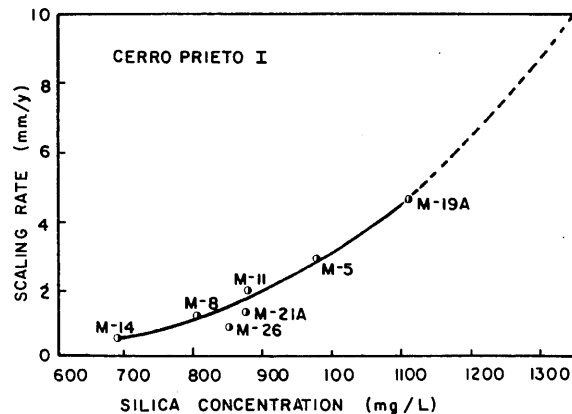


Figure 8. Maximum scaling rate on the disposal brine pipes at Cerro Prieto I.

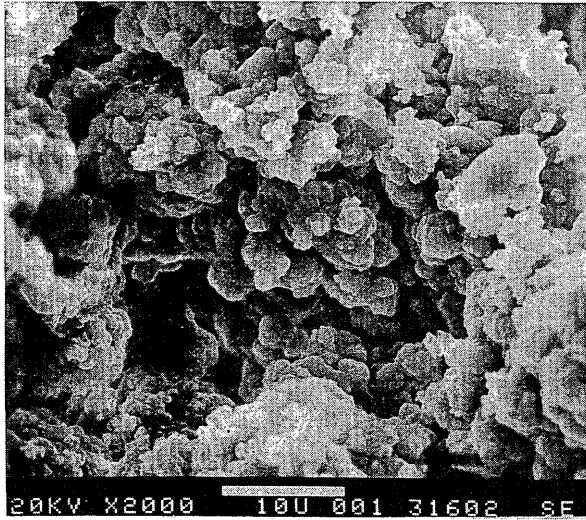


Figure 9(a). Micrograph (SEM) of scale deposited from brine of well M-19A.

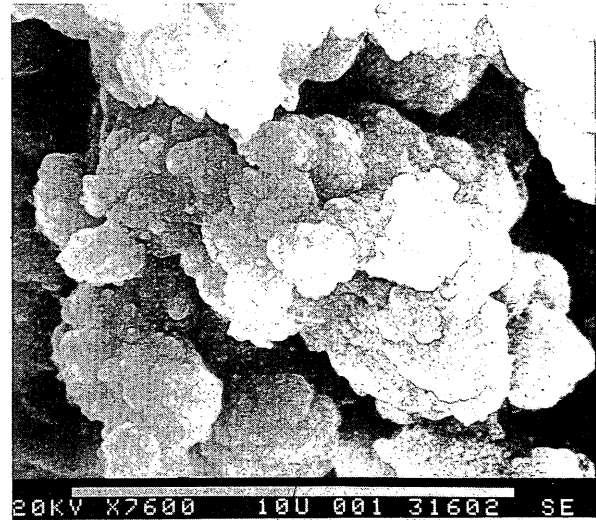


Figure 9(b). Same sample as Fig. 9(a), 7500X.

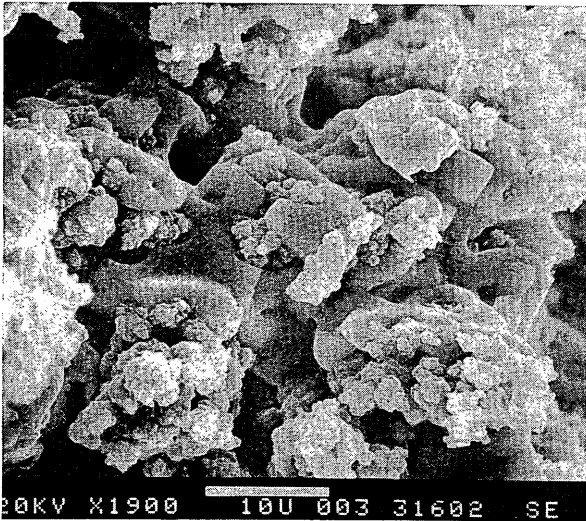


Figure 10(a). Micrograph (SEM) of scale deposited from brine of well M-53.

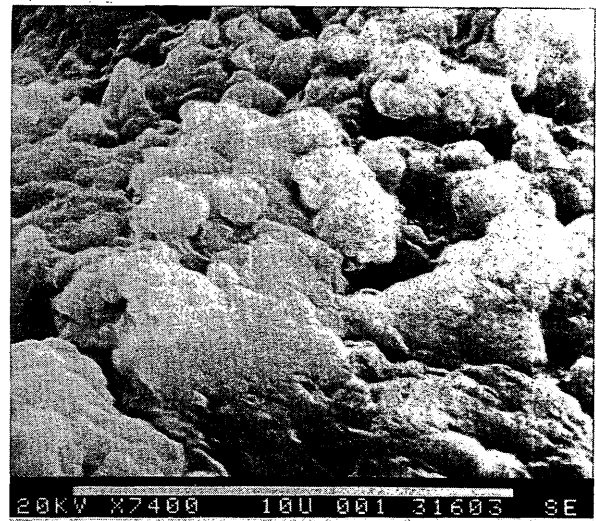


Figure 10(b). Same sample as Fig. 10(a), 7500X.

Organic Inhibitors

A number of tests, both in the laboratory and in the pilot plant were run in order to test the capacity of some organic compounds as inhibitors of silica scale. The dosage of the products tested varied in a range of 0-40 ppm. In general the results from the tests conducted were not satisfactory, the tendency to deposit silica was higher using inhibitors in comparison to original

brine under similar conditions. The only exception was with a product from the Betz Company with a trade name GCP-129. In this case we experienced a reduction of about 20 % in the deposition rate. The test conditions were:

Well No.:	M-53
Brine pressure:	42-46 psig
Flow rate:	7,500 lb/h
Silica conc.	1,352 ppm
Period of time:	24 h.

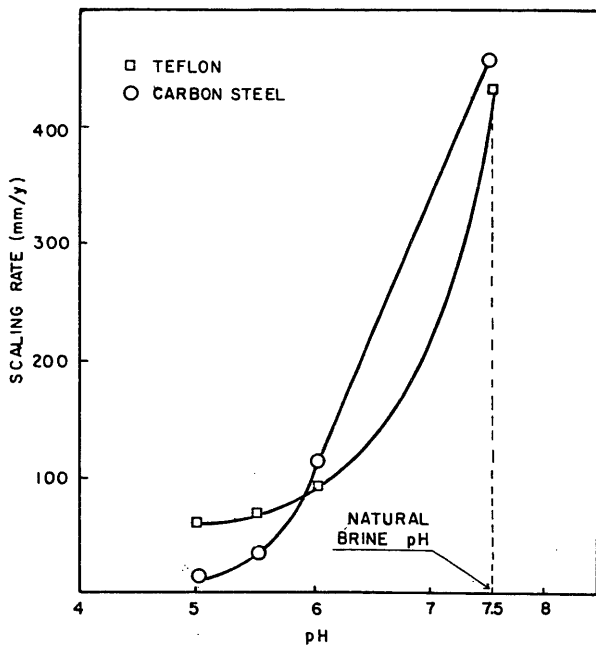


Figure 11. Scaling rate vs. pH

Hydroblasting

The objective of this test was to determine the technical and economical feasibility of this method to remove hard silica scale deposited on disposal brine lines. Two hundred feet of 3/4 inches of hard silica scale were cleaned using over 10,000 psig of water pressure at a mean rate of 30 ft/s. The test was conducted by Imperial Geothermal Services, Inc. The cost of this scale control method is a little high, but in some special case it is competitive. The fundamentals of this method are shown in Figure 12.

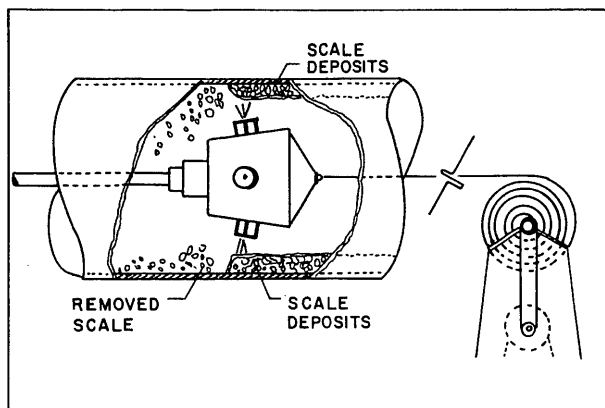


Figure 12. Fundamentals of hydroblasting method of scale control.

Chemical dissolution

Dissolution of scales was tested at Cerro Prieto in both laboratory and pilot plant facilities. Two types of scale samples were used: a) Scales deposited in production wells, and b) Scales deposited in process equipment. In the latter, amorphous silica was the main component. The silica in the production well was deposited as complex silicates. The chemical compounds tested to dissolve scales were: NaOH, KOH, HCl, Ammonium Bifluoride solutions, and mixtures of HCl and HF. The laboratory tests were run in an autoclave at temperatures from 80 °C to 150 °C. In the case of amorphous silica deposited in process equipment like tanks and valves, the best results are presented in Table 3. The objective of scale dissolution of amorphous silica was to clean valves or special parts of process equipment and help hydroblasting by softening hard silica scales.

In the case of dissolution of scales from well production pipes the results indicate that complex silicates can be dissolved by using HCl and mixtures of HCl and HF. 70-80 % of dissolution were obtained. An additional advantage of these acids is their high capacity to dissolve calcite, also present in some Cerro Prieto wells. Caustic compounds presented low dissolution rates. Preliminary engineering calculation indicates that this scale control method has some advantages over the conventional method: (a) Shorter period of maintenance (1/4), (b) Lower cost (1/3), and (c) Higher flow recovery rate.

Table 3. Chemical dissolution of amorphous silica scales.

Temperature (°C)	% of Dissolution		
	NaOH	KOH	NH ₄ HF ₂
80	10	8	59
100	40	27	66
150	99	99	82

Removal of silica

Geochemical and reservoir engineering studies have shown the convenience of reinjection of the Cerro Prieto disposal brine. Because the high scaling tendency of this brine, reinjection is only possible if the colloidal silica is removed prior to reinjection. Also in this case laboratory and pilot plant tests were performed to select the process to

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remove colloidal silica (Hurtado, et al. 1989). Figure 12 shows the flow diagram of the pilot plant tested at Cerro Prieto. The results indicate that the addition of 20-40 ppm of lime to flashed and aged brine for 10-20 minutes yields a clarified brine relatively low in suspended solid (10-30 ppm) for an overflow rate of 1.1 GPM/ft². Preliminary engineering calculations indicate that the treatment of 6,000 klb/h of disposal brine from Cerro Prieto I power plant costs 1.1 mills/KWH.

Other Studies

The Electric Power Research Institute and Instituto de Investigaciones Eléctricas signed a cost shared agreement to test at Cerro Prieto a flash crystallizer separator designed and built by EPRI. The test program was carried out from 1986 to 1989, and the test results indicate that silica desupersaturation can be achieved in such equipment if the concentration of seed is kept over 10%.

A short program related to the fluidized bed method of scale control was partially completed with promising results. Unfortunately the test program suffered an interruption due to problems with the brine source (a sudden decrease in the well output). The overall heat transfer coefficient (U) was kept constant (Test time= 8h) between 1800 and 1900 BTU/ft²-°F.

STUDIES UNDER DEVELOPMENT

Currently, three scale control studies are under development, (1) Chemical modeling of scaling, (2) Studies of scaling phenomena at the reservoir production zone, and (3) Brine treatment for Cerro Prieto IV reinjection.

CONCLUSIONS

The most important results from the scaling studies conducted at Cerro Prieto can be summarized as follows:

1. The selection of the process variables from pilot plant test have been successful. The predicted scaling rate at the evaporation station of Cerro Prieto I five unit has been confirmed.
2. The use of chemical methods to clean special sections of process equipment like sight level indicators, has been implemented with success.

3. The process developed for brine treatment is going to be used, with minor modifications, at Cerro Prieto IV.

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