LINE MINE: A PROCESS FOR MITIGATING INJECTION WELL DAMAGE AT THE SALTON SEA, CALIFORNIA (USA) GEOTHERMAL FIELD

Darrell L. Gallup, John L. Featherstone, Jessie P. Reverente, and Philip H. Messer

Unocal Corporation
P.O. Box 76, Brea, CA 92621 USA

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ABSTRACT - Injection wells that, reinject spent brine at the Salton Sea Geothermal Field can suffer damage as a result of iron silicate and heavy metal scale deposition in the wellbore and formation. A process, known as Line Mine, has recently been developed to polish brines and collect scale deposits at the surface just prior to injection. The process consists of passing brine, exhibiting a pH of ~5.0, through a conduit packed with coiled, galvanized poultry wire for a time sufficient to precipitate a significant amount of iron silicate and heavy metal scales thereon. The wire packing serves to filter some siliceous suspended solids from the brine, while simultaneously removing and recovering a small amount of silver, copper, antimony and arsenic by a cementation reaction. Scale deposition downstream of Line Mine (in surface injection facilities and wellbores) is greatly reduced. The useful life of injection wells appears to be extended as a result of this brine-treatment process by reducing wellbore tubular scaling and reservoir formation damage.

1. INTRODUCTION

The solubility of most aqueous species decreases when solution temperatures and pressures are decreased. This is particularly true for species that are near their saturation concentration in solution. An example of such a solution is geothermal brine which may be flashed to steam in a power plant or industrial process. Flashing of geothermal brine is often accompanied by the formation of scale deposits on surfaces of fluid-handling equipment. An especially troublesome, scale-forming component of geothermal brine is silica. At the Salton Sea Geothermal Field located in southeastern California (USA) (see Figure 1), flashing of high temperature, hyper-saline brine (to produce steam for power generation) results in massive deposits of an iron-rich silica scale. Iron silicate scale deposition rates have been observed to exceed 30 cm per year in brine disposal piping and injection wells at the Salton Sea field (Gallup, 1989).

Control of iron silicate scale deposition at the Salton Sea field has led to the development of ~240 MWe of power production over the past decade. Iron silicate scaling is controlled mechanically in most resource production facilities employing a combination of seed crystallizers and reaction clarifiers (Featherstone and Powell, 1981). Brine treatment with acid has recently been demonstrated to chemically control this rather unique type of scale at one production facility (Hoyer, et al., 1991).

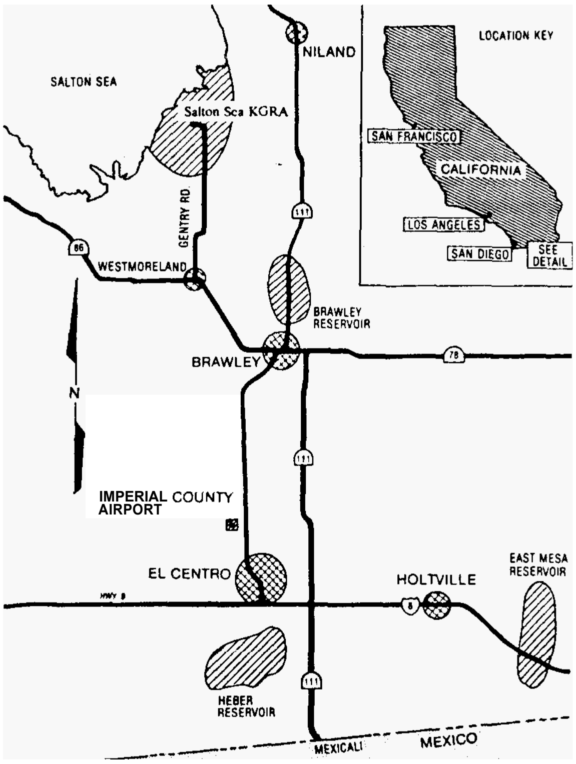

Figure 1. Salton Sea Geothermal Field

In addition to amorphous iron silicate, under certain brine processing conditions, other crystalline scale components may be observed. Brines reduced in temperature below about 150°C deposit barium sulfate and calcium fluoride. Copper arsenide and silver antimonide scales form on mild steel surfaces below about 125°C and 150°C, respectively. Acidified brine typically deposits more of these heavy metal scales than un-acidified brine (Gallup, 1992). By contrast, commonly in geothermal systems, silver and copper are deposited in scales as sulfides (Skinner, et al., 1967; Clark and Williams-Jones, 1990). These crystalline scales tend to deposit from post-flashed brine in injection brine piping, injection wellbores and near-wellbore reservoir rocks. Additional formation damage may result from invasion of suspended solid precipitates (Primarily iron silicate particles) present in injection brine into permeable sections of the reservoir (Watkins, et al., 1979).

2. DEVELOPMENT OF THE LINE MINE PROCESS

A research program was designed to mitigate the deposition of barium sulfate, calcium fluoride, the heavy metal compounds, and residual iron silicate in brine disposal piping and wells. Mixtures of these scale components typically deposit in the brine disposal systems downstream of crystallizers/clarifiers and acid injection at a rate of 2 cm per year or less. Processes for controlling the deposition of these scale components, together with removal of brine suspended solids, were investigated. Suspended solids in injection brines are present at a concentration of < 20 mg/kg and consist primarily of iron silicates spheres ranging in size from 2 - 12 microns in diameter.

Table 1 presents an analysis of a typical Salton Sea brine corrected to reservoir conditions. The brine consists primarily of sodium, calcium and potassium chlorides. Additionally, various metal ions, anions and dissolved gases are present in the brine. Iron silicate, resembling the mineral, hisingerite, deposits from the brine downstream of production wells (Gallup and Reiff, 1991). The composition of iron silicate scale is shown in Table 2. After flashing and processing brine with crystallizer/clarifier or pH modification technologies, the scale compositions in injection piping and wells changes appreciably (see Table 3). Injection scales become enriched in crystalline species, especially heavy metal compounds. Moreover, enhanced metal deposition, particularly silver, has occurred in the presence of various reducing agents injected into brine (Gallup and Jost, 1991).

Table 1. Salton Sea Reservoir Brine Composition
(pH – 5.5; Eh –-220 mV)

Analyte	mg/kg	Analyte	mg/kg	Analyte	mg/kg
Ag	1	Mg	52	Br	85
As	10	Mn	760	Cl	128,400
B	300	Na	49,900	F	16
Ba	190	Pb	70	I	19
Ca	22,700	Rb	51	SO_4	105
Cu	4	Sb	1	CO_2	500
Fe (Fe^{3+})	700 (12)	SiO_2	480	H_2S	7
K	12,300	Sr	380	NH_3	375
Li	165	Zn	280	TDS	220,600

Table 2. Iron Silicate Scale Composition

Mineral Mode	Wt%
Al_2O_3	1.5
CaO	1.0
Fe_2O_3	42.0
Mn_2O_3	1.0
SiO_2	39.5
$-H_2O$	15.0

Table 3. Injection Piping - Line Mine Scale Compositions

Mineral Mode	Crystallizer/ Clarifier. 105°C	pH Modification, 180°C
Ag (present as Ag_xSb_y)	2	7
As	9	1
Cu (present as Cu_xAs_y)	30	2
Fe_2O_3	4	11
Sb	6	14
$BaSO_4$	17	0
CaF_2	3	0
SiO_2	21	51
$-H_2O$	8	14

It was postulated that scale deposition in injection wells could be mitigated by collecting deposits in surface equipment. Enhanced collection of scale on the surface would require deposition on a substrate with high surface area. The process would have to be simple, cheap and easy to operate. Secondary benefits of the process would be filtration of brine to remove suspended solids (brine polishing) and recovery of valuable metals. The proposed process was given the name, Line Mine.

3. PILOT TESTING OF THE LINE MINE PROCESS

To develop a process to protect injection piping and wells from plugging with scale enriched in the crystalline compounds, to polish the injection brine, and to recover valuable metals from the brine, a pilot plant test apparatus was constructed and operated with a slipstream of injection brine from a resource production facility. Figure 2 is a diagram of the test apparatus. A slipstream of injection brine exiting a clarifier was sent to the pilot plant at a rate of about 76 L per minute, at a temperature of about 105 °C and pressure of about 6 bars. The pilot plant utilized in the tests consisted of a 5 cm-diameter upstream corrosion/scale collection conduit and a static mixing conduit constructed of mild steel. The static mixer was a 30 cm-long helix constructed of stainless steel. Located just upstream of the mixer was a chemical (acid) injection nozzle to allow the pH of the brine to be modified. Downstream of the mixing conduit was a 8 cm-diameter section of conduit that was packed with various scale collection substrates. In some tests, brine exiting the packed conduit was filtered through a cloth cartridge filter (location 1B, Figure 2).

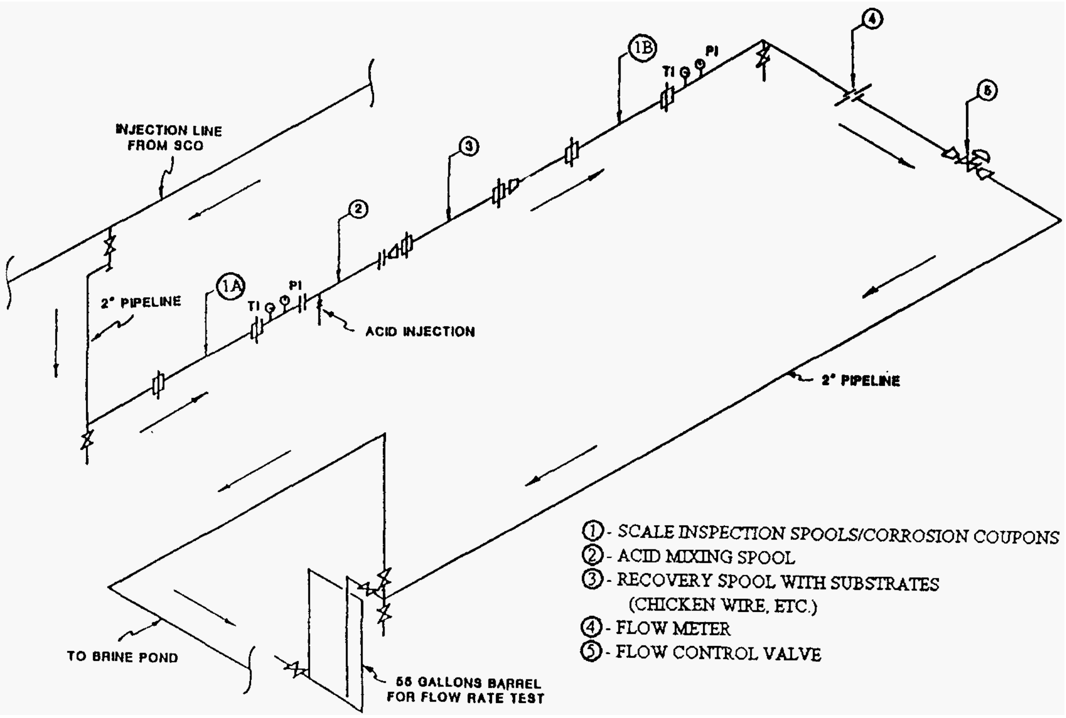

Figure 2. Pilot Test Apparatus

The brine then was passed through a second corrosion/scale inspection conduit before being discharged to a drain. The residence time of the brine in the test apparatus was about one minute. Tests usually lasted for about 120 hours.

At the conclusion of the tests, the two inspection conduits and the packed spool (and cartridge filter) were removed and inspected. Scale deposits were mechanically scraped off the conduit walls and packing material, washed with water to remove entrained brine, dried overnight in a forced-air oven (at 100°C), weighed, and analyzed. In this manner, packing materials could be compared for scale collection, and the effect of scale collection on control of deposition in simulated injection piping and reservoir formation could be determined.

The results of selected pilot tests of 120 hours duration are given in Table 4. This cross-section of pilot tests compares upstream, packed conduit and downstream scaling rates with various substrates installed in the packed, agitation collection conduit. Substrates compared in Table 4 include mild steel ball bearings, coiled, galvanized poultry wire, coiled lead wire and coiled copper wire. The tests also compared scale collection with acidified (pH 4.9) and unacidified (pH 5.4) brines. Acidification was achieved by injecting 20 ppm of concentrated hydrochloric acid into the brine at the mixing conduit. In tests with both unacidified and acidified brine, coiled poultry wire collected the most scale in the packed conduit. This packing also yielded some of the best downstream scale mitigation and metal recovery results. Further, in tests with these packings, filtration of brine suspended solids was observed. In general, ball bearings alone, and lead and copper wire packings gave poorer results than iron poultry wire packings.

Table 4. Comparison of Line Mine Pilot Test Results

Test #	Metal Packing & Brine Treatment	Upstream Scaling Rate, mg/kg brine flow	Packed Conduit Scaling Rate. mg/kg	Down-stream Scaling Rate, mg/kg	Silver Recovery troy oz/ton	Gold Recovery troy oz/ton	Platinum Recovery troy oz/ton
1	None	0.156	0.182	0.203	84	<0.0001	<0.0001
2	Mild steel ball bearings, not acidified	0.098	0.717	0.132	408	0.041	0.0035
3	Ball bearings, acidified	0.216	0.945	0.113			0.0023
4	Iron (poultry) wire. not acidified	0.166	1.970	0.110			0.0018
5	Poultry wire, acidified	0.106	1.990	0.063			0.014
6	Lead wire. not acidified	0.177	1.454	0.120			0.016
7	Lead wire, acidified	0.180	1.249	0.039		0.003	0.017
8	Copper wire, not acidified	0.156	1.114	0.168	83	0.002	0.001
9	Copper wire, acidified	0.094	0.580	0.104	318	0.001	0019

In several tests, cartridge filters were installed in the pilot test apparatus downstream of the packed conduit to simulate injection formation. The fabric filters had nominal mesh sizes of 15 - 20 microns. In the absence of a wire-packed section (unacidified brine), the filters completely plugged after 24 -48 hours of flow. By comparison, the filters located downstream of galvanized, poultry wire-packed sections (brine was acidified to pH 5.0) did not plug even after 120 hours. This data implies that brine treated with acid and wire packing may not damage injection formations as rapidly as untreated brine. This may indicate that an acidification process coupled to packing treatment may extend the life of injection wells by as much as three times.

4. COMMERCIAL OPERATION OF THE LINE MINE PROCESS

Based on encouraging results of the pilot tests described above, commercial Line Mine processes were installed at three resource production facilities at the Salton *Sea* field. At the first facility which utilizes crystallizer/clarifier silica scale control technology, coiled, galvanized poultry wire (corresponding to Run #5, Table 4) is packed into a pipe conduit located upstream of a deep injection well. The pipe conduit measures about 50 cm in diameter by 15 meters in length. Brine at 105°C is first acidified with concentrated hydrochloric acid to reduce the pH from about 5.4 to about 4.9. The acidified brine is then passed through the packed conduit at a flow rate of about 455,000 kg per hour. The residence time of the brine in the packed conduit is estimated to be several minutes. Under normal operating conditions, the packing does not plug with scale for about 30 days, at which time the pressure drop across the packing becomes excessive. Brine flow is diverted to a parallel packed conduit for continuous operation, and the scaled wire packing is removed and replaced with fresh wire. Typically, the scaling rate upstream of the acid injection point and wire-packed conduit is 1.3 cm per year. Downstream, the scaling rate is reduced to less than 0.6 cm per year, resulting in a > 50% reduction in scaling. The packing removes an average of 30 metric tons of scale per year that would otherwise deposit in the injection well. This scale, shown in Figure 3, exhibits a composition similar to that observed for crystallizer/clarifier brine (see Table 3).

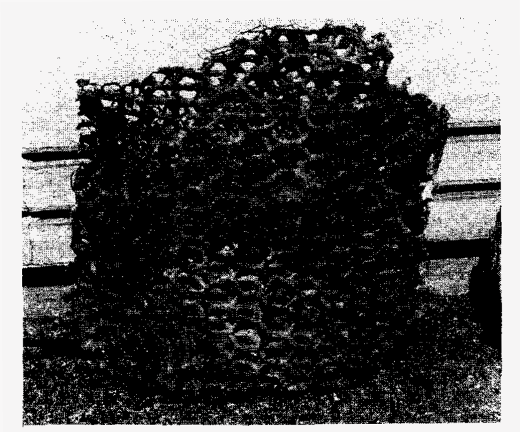

Figure 3. Photograph of Line Mine Scale from Commercial Operation

The second resource production facility utilizes pH modification scale control technology. Injection brine from this facility enters the Line Mine installation at a temperature of about 180°C and pH of 4.9. This Line Mine operates similar to that described above, except that the length of the packed spool is only 9 meters and 635,000 kg per hour of brine is allowed to pass through the wire packing. Scaling rates upstream and downstream are similar to those detailed above, but the scale composition is different (see Table 3). The packing removes about 25 metric tons of scale per year that would otherwise deposit in the injection well.

At the third production facility, 1,640,000 kg per hour of 109°C brine from a clarifier system is treated through groups of parallel Line Mines. It is estimated that these Line Mines collect 90 metric tons of scale per year. Brine at this location is not acidified due to its natural pH of 5.0 (corresponding to Run 4, Table 4). Scale reduction results across the wire packed conduits are similar to the above cases. The composition of the scale is the more copper-rich variety shown in Table 3.

Suspended solids analyses of crystallizer/clarifier brines across the Line Mines have shown that the wire packings act as a filter. An average of 28 ± 3 ppm suspended solids (primarily iron silicate particles) is present in brine entering the Line Mine installation. Downstream of Line Mine, suspended solids concentrations average 21 ± 2 ppm. Thus, Line Mine typically reduces suspended solids concentrations in brines by 25% over the life of a packing.

Acidification of brine at the first two facilities is expected to enhance corrosion of brine-handling equipment. To determine the effect of acid injection on brine corrosivity, corrosion coupon tests were conducted at the Line Mine that treats lower temperature brine (Facility 1 above). Racks containing 5 x 10 cm metal coupons spanning a range of compositions were placed upstream of the acid injection point (and poultry wire packing) and downstream of the packed conduit. During the test, 20 ppm of concentrated hydrochloric acid was injected upstream of the packing to reduce the brine pH from 5.4 to 4.9. After 33 days of exposure, the test coupons were examined, and an estimate of general corrosion rates was made based on weight loss measurements. Pitting corrosion was also estimated based on the deepest pit found on a given coupon.

The results of the corrosion tests are presented in Table 5. These results surprisingly show that acidified brine (pH 4.9) is less corrosive toward most materials after passing through Line Mine than prior to acidification (pH 5.4). The mild steel coupon did

Table 5. Corrosion Test Results

Alloy	Upstream of Acid and Line Mine General, mpy	Upstream of Acid and Line Mine Pitting, mpy	Acidified, Downstream of Line Mine General, mpy	Acidified, Downstream of Line Mine Pitting, mpy
AISI 1018 mild steel	277	480	250	290
AL 29-4-2* ferritic stainless	18.7	84	0.3	6
316 L stainless	12.1	24	0.1	12
2205 duplex stainless	11.7	48	0.6	24
2507 duplex** stainless	1.9	36	0.3	<6
SM 2250	1.4	0	0.4	0
SM 2035	0.8	0	0.4	0
904 L stainless	0.6	6	0.4	0
Carpenter 20Cb-3	0.4	12	0.1	6
Inconel 625	0.3	0	0.2	0

* 29% Cr. 4% Mo. 1% Ni

** Sandvik 25% Cr, 7% Ni, 4% Mo, 0.3% N

not show a dramatic improvement in corrosion, but all of the alloy coupons tested showed reduction in corrosion rates of at least 30% and an average reduction in excess of **50%.** Apparently, Line Mine actually reduces corrosion in the presence of acidified brine perhaps by removing corrosive metal ions.

5. DISCUSSION OF LINE MINE PROCESS

The Line Mine process installed at the Salton Sea field has proven useful for inhibiting the deposition of iron silicate and other scales from spent injection brine. Line Mine filters a portion of suspended solids entrained in the brine, and also promotes the recovery of silver and other precious and base metals within the existing brine-handling process. The corrosivity of brine may also be reduced by the process (Gallup, *et al.*, 1992a, 1992b, 1992c, 1993). Scale deposited on the wire packing may be removed by mechanical or chemical (dissolution) means for disposal or recovery of the precious and base metals. Because Line Mine scales contain elevated levels of heavy metals, environmental and safety requirements must be met in handling and disposal of such scales. During initial operation of the Line Mine process, the scales were contaminated with NORMs (naturally-occurring radioactive materials) in the form of radium-substituted barium sulfate. However, a process was eventually developed to inhibit NORMs deposition in these scales (Gallup and Featherstone, 1993).

Wire packings employed in the Line Mine collection spool provide additional surface area (beyond simple conduits) on which scales may preferentially deposit. The wire serves to inhibit the formation of iron silicate scale and to mitigate corrosion by a reduction reaction with ferric ion in the brine (Gallup, 1993). Ferric ion species in the brine have been shown to be responsible for the formation of ferric silicate scale. Wire acts as a sacrificial reducing agent to convert ferric ion to the less reactive and corrosive ferrous state:

$$2\,Fe^{3+} + Fe \rightarrow 3\,Fe^{2+} \qquad (1)$$

Wire packings appear to remove precious and base metals from brine via cementation-type, galvanic reactions (Maimoni, 1982; McKibben, et al., 1990). So long as the packing material is higher in the electromotive series than silver, high concentrations of precious and base metals can be recovered from the brine (Brown and Roberts, 1988). Although exact mechanisms of metal deposition reactions are unknown, it appears that silver and copper ions are reduced to their elemental states:

$$2\,Ag^{+} + Fe \rightarrow 2\,Ag + Fe^{2+} \qquad (2)$$

Silver and copper in the scales recovered in the Line Mine packed spool are codeposited with antimony and arsenic, respectively. Formation of silver-antimony and copper-arsenic compounds appears to increase the overall recovery of silver in the process. In the Line Mine process, the anodic reaction appears to be the oxidation of iron and the cathodic reaction is the reduction of silver and antimony to form silver-antimony alloys (a mineral phase near dyscracite, Ag_3Sb). For copper and arsenic, the half-reactions are probably similar. A plausible reaction mechanism for the deposition of dyscracite in the Line Mine process is:

$$3\,Fe + 3\,Ag^{+} + H_3SbO_3 + 3\,H^{+} \rightarrow Ag_3Sb + 3\,Fe^{2+} + 3\,H20 \qquad (3)$$

The free energy of Reaction 3 appears to be extremely favorable. Thermochemical calculations using the computer program, EQUILIB, yield -AG values ranging from −130 to 145 Kcal at Line Mine operating temperatures (104 - 200°C). EQUILIB utilizes input $\Delta H°_f$, $\Delta G°_f$, and C_p data to generate AH and ΔG for chemical reactions by the integrated Gibbs-Helmholtz equation. Most of the input data were obtained from Lange's Handbook of Chemistry and NBS data. Some of the C_p values had to be estimated, and in those instances, Kopp's Rule was employed. All of the heat capacities were assumed to be independent of temperature.

The galvanic reactions shown above appear to be enhanced when turbulent brine flow conditions are achieved in the presence of high surface area wire and piping. Wire packing is useful for generating these turbulent, high surface area conditions. It is interesting to note that very little copper-arsenic compound deposits from higher temperature, pH modified brine compared to the lower temperature clarified brine. That significant copper precipitation occurs from low temperature brine implies that its deposition is temperaturedependent and the copper-arsenic compounds are more soluble at higher temperature (Weeks, 1923).

As shown in Reaction 3, acidification of brine should assist in driving precious and base metal deposition in the Line Mine apparatus. Acidification of brine also slows silica precipitation reaction kinetics. At Salton Sea, general practice is to reduce the injection brine pH to about 5.0 to inhibit siliceous scaling and to enhance metal recovery. It is preferred to acidify Salton Sea brine with hydrochloric acid; hydrochloric acid is the most compatible mineral acid available with chloride-laden Salton Sea brine.

Even though the reduction in brine pH is carefully controlled, it would normally be expected that acid-treated brine would have a substantially greater corrosive effect on ferrous metal components downstream of the acid injection point. Surprisingly, across the Line Mine apparatus, just the opposite occurs. Brine treated through Line Mine is generally less corrosive (in spite of acid addition and a decrease in pH of nearly *0.5* units) than it is before treatment. It is believed that the decreased corrosion rates on downstream metal components is related to the removal of naturally-occurring ferric iron from the brine as it passes through the wire-packed conduit. However, we recognize that other reactions may take place in the metal packing that reduces the corrosivity of the brine.

The primary purpose for developing the Line Mine process is to polish brine as a means of extending injection well life and reducing maintenance demands on surface injection facilities. The enhanced quality of injection brine greatly reduces fouling of surface injection facilities (pumps, valves, orifice meters, probes, etc.) with scales. Wellbore scaling rates should be reduced by removing over 135 metric tons per year of scale on the surface that would otherwise deposit in the wellbores. Filtration of brine by the wire packing reduces the amount of siliceous suspended solids being sent to the geothennal reservoir by over 60 metric tons per year.

The Line Mine process was operated by Unocal at the Salton Sea field for nearly 3 years prior to the sale of this asset in early 1993 to Magma Power Company. Unfortunately, injection well workovers were typically performed by Unocal every 2 - 3 years, and sufficient data had not been obtained at the time of the asset sale to fully determine the effect of the Line Mine process on extending injection well life. However, it seems plausible that keeping –60 metric tons of suspended solids per year and –135 metric tons of scale per year from depositing in 7 injection wells utilized by Unocal at the field would somewhat extend the period of time between well workovers (drill out of scale).

6. CONCLUSIONS

A process, known as Line Mine, has been developed to inhibit the precipitation of undesirable scale from injection brine at the Salton Sea geothermal field. Protection of injection wells from premature plugging with scales is the primary purpose of the process. This process enhances the deposition and recovery of potentially valuable metal-containing scale. Line Mine filters some suspended solids from the brine and also reduces the corrosivity of the brine toward ferrous metal components downstream. Line Mine collects and removed nearly 30 metric tons of scale and solids per year *in surface equipment* that would otherwise deposit in a given injection well. It appears that this process may extend the useful lifetime of injection wells by reducing wellbore scaling. Furthermore, the process is expected to reduce the potential for reservoir formation damage by scaling and solids invasion,

7. ACKNOWLEDGEMENT

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