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CONTROL OF NORM DEPOSITION FROM SALTON SEA GEOThERMAL BRINES

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ABSTRACT

Processing of Salton Sea geothermal brines for silicate scale control, utilizing crystallizer-clarifier technology, produces solid wastes contaminated with NORM (naturally-occurring radioactive material). Radium-226 and radium-228, present in concentrations ranging from 250 - 400 pCi/g, co-precipitate with barium sulfate in clarifier sludges and injection system scale deposits at temperatures below ~160°C. A patent-pending process has recently been developed to inhibit NORM deposition in sludges and scales that does not adversely affect stabilization of brine with respect to silica. Low dosages of commercially-available scale inhibitors are injected into brines to reduce radium concentrations in sludges and scales below 15 pCi/g, an anticipated NORM regulation for solid wastes. The inhibitors may disperse precipitates in clarifiers requiring the use of cationic flocculants for final injection brine polishing (i.e., settling of particles and stabilization of slowly precipitating silicates.

INTRODUCTION

Efficient extraction of energy from high temperature, hypersaline brines encountered at the Salton Sea geothermal field, located in southeastern California, has been hampered by severe scaling (scaling rates exceeding 30 cm per year) and corrosion. In particular, deposition of massive amounts of iron-rich silica scale in production wells, surface equipment, and injection wells required successful implementation of novel scale inhibition processes to allow the development of efficient flash power plants (Featherstone and Powell, 1981). Over the past decade, crystallization/clarification technology has proven to be an excellent mechanical solution to exploiting the Salton Sea resource by carefully controlling precipitation of iron-rich silica (Newell, et al., 1989). A chemical process for inhibiting the deposition of this scale by modifying the brine pH with low dosages of acid has also shown promise in a resource production facility at the field (Hoyer, et al., 1991).

Iron-rich silica scaling is exacerbated as brine temperatures and pressures decrease during flashing to produce steam for the power plants. As brine is flashed, iron-rich silica becomes supersaturated and begins to grow rapidly as hard, brittle scale.

De-supersaturation of silica is accomplished in the crystallizer-clarifier process by seeding brine with re-cycled iron silicate particles. Iron-rich silica sludge in the form of sub-rounded to rounded particles ranging in diameter from about 5 - 20 µm is separated from brine in a series of clarifiers. Brine exiting the clarifiers exhibits very little tendency to form scale deposits (scaling rates are typically reduced to < 1 cm per year) and is disposed in deep injection wells (Featherstone, et al., 1989). Figure 1 is a schematic diagram of a Salton Sea resource production facility that utilizes the crystallizer-clarifier brine treatment process.

Iron-rich silica sludge is continuously removed from the clarifiers. About 600 mg of sludge is formed per kg of brine treated in the crystallizer-clarifier process. Under normal operating conditions, ~65 wt% of the sludge is hydrous iron-rich silica, ~3 wt% is fluorite (CaF₂) and ~31 wt% is barite (BaSO₄). Co-precipitated with barite is a little strontium and NORM (in the form of Ra-226 and Ra-228 radionuclides). Sludge removed from the clarifiers is de-watered (Gallup and Featherstone, 1990) and disposed in waste repositories or beneficially used in road/levee construction materials (Whitescarver, et al., 1988).

NORM DEPOSITION

Geothermal fluids produced from the Salton Sea geothermal field are characterized by hyper-saline brines exhibiting total dissolved solids concentrations (TDS) ranging from 15 to 30 wt%. These brines, produced at temperatures ranging from 230 to 330°C, consist primarily of dissolved sodium, potassium and calcium chloride salts. The primary dissolved gases in the brines included CO₂, NH₃ and H₂S.

Dissolved silica and iron concentrations in brine are about 450 and 750 mg/kg, respectively. Iron, in both the ferric and ferrous oxidation states, reacts with silicic acid oligomers to form iron-rich silica scales and sludges (Gallup and Reiff, 1991). Iron-rich silica begins to precipitate from brine below about 200°C (Gallup, 1989). Produced brines also typically contain ~200 mg/kg of barium, ~100 mg/kg of sulfate, and ~20 mg/kg of fluoride. Barium sulfate is predicted to reach saturation in concentrated Na-K-Ca-Cl brine at about 160°C using a scale prediction model (Jost, 1978). Barium sulfate and calcium fluoride exhibit prograde solubility, so as Salton Sea brine continues to decrease in temperature upon flashing through the crystallizers and clarifiers (to an injection
Several years ago, we began an investigation designed to solve the problem of NORM deposition and disposal at the Salton Sea field. Using a systematic and scientific approach, the sources of radioactivity in the sludge and scale deposits were determined. Then, the chemistry and processes responsible for NORM deposition were elucidated. With the knowledge gained in these initial studies, several potential methods to mitigate NORM and unwanted BaSO₄ and CaF₂ deposits in the geothermal operation were investigated. Mitigation methods were constrained by the desire to develop a process that would be compatible with operation of existing resource production facilities wherein iron-rich silica crystallization and brine clarification/stabilization/polishing could continue unaltered. Studies then focused on methods to dissolve or inhibit NORM deposition from Salton Sea brines.

**Dissolution.** Filter cake sludges from the Salton Sea clarifiers were examined for leachability of NORM. In laboratory tests, sludges and concrete blocks containing sludge were leached for up to 30 days with distilled water (simulated rain water) and Salton Sea water (simulated worst-case groundwater). NORM was found to be completely insoluble in these leaching experiments. Groundwaters sampled around the Salton Sea geothermal plants where sludge had been used beneficially in road and levee construction showed no nuclide concentrations above natural background, confirming the laboratory results.

Attempts to leach NORM from sludges with a variety of chemical solvents were not particularly successful. Acids and bases were ineffective in dissolving NORM. Commercially-available barium sulfate dissolvers (chelates and converters in basic solution) were somewhat successful in leaching about 25% of NORM and BaSO₄ from sludge even under very rigorous reaction conditions (high temperatures, long leach times, stirring, etc.).

Bio-leaching of NORM has recently been proposed as a practical method to reduce radioactive waste volumes, especially in regard to geothermal sludges (Premuzic, et al., 1991). To date, we have not investigated this potential option. However, we recommend that further investigations be conducted to determine the feasibility and cost effectiveness of bio-leaching processes for de-contamination of geothermal wastes containing NORM.

**Inhibition.** A variety of scale inhibitors have been used in the petroleum industry to successfully inhibit barite and fluorite deposition in wells, piping and produced water handling equipment (Vetter, 1972). When barite is properly inhibited, NORM deposition is also expected to be mitigated (Smith, 1987). Inhibitors that have found application in control of barium sulfate scales include phosphonates, polyacrylates, polymalates, etc. Unfortunately, there is much disagreement and poor understanding concerning the effectiveness of these inhibitors, optimum dosage requirements and reaction mechanisms involved in these inhibition reactions (Tomson, 1983).

In general, inhibitors that have been used to control barium sulfate and NORM scaling in the petroleum industry are highly-charged, polymeric organic compounds. These inhibitors will impart charges on particles resulting in dispersion of solids. Zeta potentials of the siliceous solids precipitated in the crystallizers and clarifiers at Salton Sea.
various flocculant formulations were also tested in the jar experiments. Several mildly cationic flocculants were able to overcome the adverse reaction of the inhibitors on the suspended solids, causing increased dispersion and poor settling (upsets) in clarifiers. In this regard, flocculants are injected into clarifiers to gather and settle suspended solids for polishing of injectate brines. Inhibitors that disperse the siliceous precipitates are expected to deleteriously affect flocculated clarifier operation. Clearly, a method that prevents or inhibits radioactive geothermal scale/slug from precipitating that does not interfere with clarifier-clarifier operation and the action of the flocculants used to settle slowly precipitating silicate species is needed.

PILOT TESTING OF INHIBITORS

Owing to the lack of understanding on the effect of inhibitors to control NORM deposition in geothermal, siliceous crystallizer-clarifier stabilization process, a series of pilot scale tests, designed to determine the feasibility of inhibitor treatment of brine for NORM deposition control, was conducted at the Salton Sea field. A slipstream of clarifier brine (105°C) was passed through a 8 cm-diameter, 0.6 cm-long scale collection pipe spool at a flow rate of 76 L per minute. Upstream of the scale collection spool, a chemical injection port and a static mixer were used to inject and mix inhibitor with slipstream brine. A variety of commercially-available inhibitors touted to inhibit barium sulfate scaling (especially in the petroleum industry) were screened for NORM, BaSO₄, and CaF₂ scale control at a constant dosage of 8 mg/kg (as-received). Typically, test durations were 120 hours.

At the conclusion of each test, the collection spool was removed and mechanically cleaned of all scale deposits. The scale samples were weighed and analyzed for major clement compositions and for radium-226 by gamma spectroscopy. In this manner, inhibitors were compared for scale control efficiencies. Table 1 presents the results of the pilot tests. Most of the inhibitors screened in the pilot tests proved to inhibit at least some NORM, BaSO₄, and CaF₂. Several inhibitors controlled radium deposition by about 90%; radium concentrations in resultant scales were reduced from about 100 pCi/g (untreated brine) to below pending NORM standards of 15 pCi/g. None of the inhibitors tested appeared to reduce residual silica scaling. In general, the more promising inhibitors contained phosphonate and acrylate functionality.

In conjunction with the pilot scale tests, the most promising inhibitors were added to jars containing fresh, flocculated clarifier brine. Flocculant present in the brine was a very high molecular weight polyacrylamide with a very slightly anionic functionality (Featherstone, et al., 1989). These treated brines were incubated in an oil bath and suspended solids in the supernatant liquids were measured following procedures commonly employed to test flocculants. Most of the inhibitors dispersed the clarifier solids, as we had expected. To combat the adverse reaction of the inhibitors on the suspended solids, various flocculant formulations were also tested in the jar experiments. Several mildly cationic flocculants were able to overcome the additional negative charge imparted on the suspended solids by the anionic, dispersing inhibitors. This latter result suggested to us that injection of an inhibitor upstream of the low pressure crystallizer (just before NORM, BaSO₄, and CaF₂ begin to precipitate) coupled with injection of a cationic flocculant into the secondary clarifier could achieve our objective of controlling NORM deposition without adversely affecting the silicate crystallization-clarification process (Gallup and Featherstone, 1993).

COMMERCIAL DEVELOPMENT OF THE NORM INHIBITION PROCESS

Inhibitor E (refer to Table 1), a polyacrylate product, was selected for initial demonstration testing at a resource production facility due to its effectiveness in the pilot tests and its low cost. The as-received polyacrylate was diluted by up to 80% with fresh water to facilitate injection into the low pressure crystallizer inlet piping. Over three months of testing, "active" inhibitor dosages were varied from 1 - 20 mg/kg. The slightly anionic flocculant that had been used successfully in the secondary clarifier for several years was replaced with a cationic flocculant to control injection brine suspended solids. Throughout the duration of the test with Inhibitor C, no inhibition of NORM or BaSO₄ in clarifier sludge was detected. However, CaF₂ deposition in sludge was inhibited by over 95%. Surprisingly, "true" scale deposits in injection piping were inhibited with respect to NORM, BaSO₄, and CaF₂ by over 75%.

Next, Inhibitor C, an acrylate co-polymer designed for high temperature applications, was tested for about 6 weeks. This inhibitor, applied similarly to Inhibitor E described above, yielded comparable results to those obtained with the polyacrylate, even over a wide dosage range. A scanning electron micrograph of clarifier sludge produced during injection of Inhibitor C into crystallizer brine, Figure 3, shows the presence of uninhibited barite rods and iron silicate spheres (compare with Figure 2). That acrylate-based inhibitors had little effect on NORM and BaSO₄ in clarifier sludge, but successfully controlled the unwanted scale components in pipe scales, suggested that products that act by inhibition mechanisms different from dispersants should be examined. Alkylaminophosphonates, that inhibit scale formation by modification of crystal growth, were subsequently demonstration-tested. Upon injection of Inhibitor B into brine, an immediate decrease of NORM, BaSO₄, and CaF₂ was detected in sludge produced from the clarifiers (see Figure 4). At dosages (as-received) ranging from 2 - 4 mg/kg, Inhibitor B rapidly and exponentially reduced the concentration of Ra-226 and Ra-228 in filter cake sludges removed from the clarifiers. The rate of NORM disappearance in the filter cake sludge exhibited first-order dependence attributed to the removal of sludge from the clarifier coupled with > 98% inhibition efficiency. After 30 days of testing Inhibitor B, Ra-226 concentrations in sludge were reduced from 400 to < 15 pCi/g. Eventually, under commercial operating conditions, Ra-226 and Ra-228 concentrations in filter cake sludges have been reduced to the 5 pCi/g range, each, employing Inhibitor B dosages of about 2 mg/kg (as-received). Figure 5 shows a scanning electron micrograph of fully-inhibited sludge that no longer contains NORM/barite rods as a result of treatment of crystallizer brine with the phosphonate inhibitor. Table 2 compares the compositions of filter cake sludges before and after NORM
During the first year of commercial NORM inhibition operations, injection of Inhibitor B has successfully inhibited NORM, BaSO₄, and CaF₂ deposition in crystallizer-clarifier sludges. A cationic flocculant added to secondary clarifier brine at a dosage of about 1 mg/kg successfully reduces the concentration of injection brine suspended solids concentrations to below 20 mg/kg (Gallup and Featherstone, 1993). Dosages of the inhibitor have been carefully optimized. When insufficient phosphate is present in brine, radioactivity (monitored daily with a scintillation counter) increases dramatically. Radium concentrations in sludge are maintained below 10 pCi/g (typically below 5 pCi/g) by injecting about 2 mg/kg of as-received Inhibitor B (about 28% active phosphate) into low pressure crystallizer brine. Fluorite scales that previously formed in atmospheric flash tank piping have also been successfully inhibited.

Application of Inhibitor B as described above has not completely inhibited NORM, BaSO₄, and CaF₂ scaling in injection piping and wells. It appears that the phosphate inhibitor adsorbs strongly to sludge particles. When sludge is removed from the clarifiers, the effective dosage of Inhibitor B in injection brine is reduced sufficient to allow post-clarifier precipitation of Fluorite scales that previously formed in atmospheric flash tank piping. When insufficient phosphonate is present in brine, injection brine at dosages ranging from 1 mg/kg successfully reduces the concentration of suspended solids in clarified geothermal brine. U.S. Patent 4,874,529.

Dosages of the inhibitor have been carefully optimized. Treatment of brine employing dual injection of Inhibitor B has completely inhibited NORM, BaSO₄, and CaF₂ scaling in downstream of the clarifiers. This dual injection of inhibitors Inhibitor B is injected into brine exiting the clarifiers. When insufficient phosphate is present in brine, radioactivity (monitored daily with a scintillation counter) increases dramatically. Radium concentrations in sludge are maintained below 10 pCi/g (typically below 5 pCi/g) by injecting about 2 mg/kg of as-received Inhibitor B (about 28% active phosphate) into low pressure crystallizer brine. Fluorite scales that previously formed in atmospheric flash tank piping have also been successfully inhibited.

Application of Inhibitor B as described above has not completely inhibited NORM, BaSO₄, and CaF₂ scaling in injection piping and wells. It appears that the phosphate inhibitor adsorbs strongly to sludge particles. When sludge is removed from the clarifiers, the effective dosage of Inhibitor B in injection brine is reduced sufficient to allow post-clarifier precipitation of NORM, BaSO₄, and CaF₂. To inhibit this post-clarifier scaling tendency, Inhibitor E was injected into injection brine at dosages ranging from 2 - 4 mg/kg just downstream of the clarifiers. This dual injection of inhibitors partially controlled injection line scaling with respect to NORM, BaSO₄, and CaF₂. To improve inhibition of these unwanted scale components in injection piping and wells, Inhibitor B is injected into brine exiting the clarifiers. Treatment of brine employing dual injection of Inhibitor B has successfully controlled scaling of the crystalline compounds throughout the resource production facility.

Owing to the low dosages of inhibitors used in the process, chemical costs to mitigate NORM and other unwanted scale components at the Salton Sea field is surprisingly low. Treatment of crystallizer-clarifier brine sufficient to generate about 70 MWe with these inhibitors costs approximately $200,000 per year. By inhibiting sulfate and fluoride precipitates, quantities of solid wastes (filter cake) requiring disposal is reduced by about 40%. This decrease significantly reduces solids handling costs. Furthermore, the NORM inhibition process potentially saves over $10,000,000 per year in estimated costs to dispose the sludge and scale in a licensed NORM repository.

ACKNOWLEDGMENTS

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REFERENCES


Figure 1. SALTON SEA UNIT Simplified Process Schematic

Figure 2. Scanning Electron Micrograph Clarifier Sludge

Figure 3. Scanning Electron Micrograph Clarifier Sludge
Figure 4. Unit 1 Norm Reduction Tests
Clarifier Underflow Ra 226 Analysis

Figure 5. Scanning Electron Micrograph
Inhibited Clarifier Sludge
### TABLE 1

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<th>Inhibitor</th>
<th>Dosage, mg/kg</th>
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### TABLE 2

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