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CONDITIONING OF GEOTHERMAL BRINE EFFLUENTS

FOR INJECTION - USE OF COAGULANTS

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TITLE: CONDITIONING OF GEOTHERMAL BRINE EFFLUENTS FOR INJECTION - USE OF
COAGULANTS

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Introduction

This report describes the use of various chemical coagulants and flocculants with spent geothermal brine for enhancing the removal of colloidal solids prior to injection. Brine at 80-85°C was obtained from the injection line of the SDG&E/DOE Geothermal Loop Experimental Facility during a period of operation with Magmamax # 1 Fluid. The solids consist primarily of an iron-rich amorphous silica and heavy metal sulfides, principally lead. Standard jar testing equipment was used to carry out the tests.

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Geothermal Loop Experimental Facility (GLEF)

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The GLEF, located near Niland in the Imperial Valley, California is a joint San Diego Gas & Electric and U. S. Department of Energy geothermal project. In operation since May, 1976, the experimental loop is a test of a 4-stage flash binary process to extract energy for electrical power generation from the high temperature, ultra high salinity brines found in the Salton Sea geothermal field. Characteristics of the GLEF operation have been documented by SDG&E in reports¹ issued bimonthly. Chemical data and characteristics of the brine, steam, noncondensable gases, scale, and solids are also described in these reports¹ and also in reports²⁻⁴ by the LLL.

GLEF Injector

An important consideration in hydrothermal development projects is the handling and disposal of spent brine. In the GLEF, spent brine is injected back into the reservoir via an injection well, Magmamax # 3. The magnitude of the injection problem can be appreciated from the operational history of the well.

Following ~1200 hours of GLEF 1-well operation, it was necessary to curtail operation in order to flush and bail out solids that had deposited in the bore of 500' of slotted liner in the injection well. After resumption of operation, injection pressures rose again. Flushing and short production periods did not measurably help. A major rework of the well was then carried out. At this time a spinner survey indicated that all of the flow was occurring in the vicinity of the upper 5' of the slotted liner. This apparently

continues to be the current injection characteristic of the well. Slotted liner strainers were installed on the surface to filter the brine. However, the strainers were of only marginal benefit since only the larger particles were trapped. The injection well pressures have risen and fallen (± 100 psi) on occasion, seemingly independent of any surface change. Magma Power, who was responsible for the above work on the injection well, has recently installed a series of Baker tanks for settling and separation of solids from the brine prior to injection. For 1-well flow, the Baker tank volume provides approximately 2 hours of holdup. In recent tests, the Baker tanks alone reduced the suspended solids concentration in the spent brine from ~ 200 ppm to ~ 50 ppm.⁵ Clearly the tanks are beneficial, but their use is recognized as only an initial step in the cleanup process.

Spent Brine Characteristics

In the GLEF process, the brine is cooled from a reservoir temperature of roughly 300°C to the process exit temperature of $80\text{--}100^{\circ}\text{C}$. Evolution and separation of the steam phase concentrates the brine by approximately 25%. Evolved with the steam is CO_2 which results in a pH elevation in the brine to ~ 5.5 from an estimated down hole value of $\text{pH} < 4.5$. All of those factors contribute in producing a supersaturated brine in metal sulfides, carbonates, and amorphous silica. Solids precipitate resulting in light to massive scaling in the GLEF and a spent brine containing from 25 to 500 ppm suspended solids. The actual concentration and chemical composition of the solids depend on various operational parameters, e.g., whether the producing

well is Magmamax # 1 or Woolsey # 1, or whether the steam condensate is recombined with the brine for injection either with or without acidification of the condensate (pH reduction by HCl addition). Examples of the concentration and chemical composition of the suspended solids in the brine effluent for 2 modes of operation are shown in Table 1.

Spent brine recombined with acidified condensate results in a much lower suspended solids concentration in the brine effluent. Irrespective of operational mode, however, silica remains in supersaturation and will presumably over time precipitate in the reservoir. This fact is demonstrated by experiments⁶ with brine effluents held in sealed bottles at 90°C. Solids, principally silica, precipitate from solution over time while dissolved silica concentration drops to saturation values. In brine supersaturated in silica in the pH range of 1-7.5, lowering or raising the brine pH from the normal value of 5.5 dramatically slows or speeds, respectively, the rate of silica polymerization and precipitation.⁷ Lowering the pH of the brine has been suggested as a means of scale and solids control,^{7,8} and is the basis for field tests involving the injection of HCl into the brine stream by LLL.²

The tests described in this report occurred during a period when Magmamax # 1 was the producing well and steam which is flashed off and condensed was not recombined with the brine. Composition of Magmamax # 1 brine is shown in Table 2. Total dissolved solids is about 20% by weight. Dissolved silica concentration drops from ~500 ppm in the brine at the production well head to ~300 ppm in the spent brine at the injection well-head. At 90°C silica will continue to precipitate, stabilizing at a

TABLE 1. Concentration and Chemical Composition of
Suspended Solids in Brine Effluent -
GLEF Operation with Magmamax # 1 Brine

ELEMENT ^(a)	NO CONDENSATE COMBINATION (CONCENTRATION, %)	ACIDIFIED CONDENSATE AND COMBINATION (CONCENTRATION, %)
Si	40.5	14
S	0.2	5.7
Pb	0.14	40.0
K	0.2	0.7
Ca	0.65	1.9
Mn	0.06	-
Fe	4.0	4.6
Cu	0.15	3.3
Zn	0.15	-
Suspended Solids Concentration, ppm	178	25
Mineralogy ^(b)	Amorphous Silica	Amorphous silica Galena, PbS possibly - Pb(OH)Cl - Pb ₃ (CO ₃) ₂ (OH) ₂

(a) by X-ray fluorescence analysis R. W. Ryon (LLL)

(b) by X-ray diffraction analysis, M. A. Chan (LLL)

TABLE 2. Elemental Composition of Magmamax # 1 Brine (Ref. 1)

Element	Concentration Mg/l
Na	37,900
K	10,000
Ca	21,300
Mg	140
Sr	440
Mn	680
Cu	0.5
Fe	280
Zn	200
Ba	140
Pb	40
Si	240
Cl	131,000

concentration of roughly 175-200 ppm in approximately 1.5 hours after leaving the final flashing stage.⁶ Brine transit time between the final stage in the GLEF and the injection wellhead is 20-25 minutes, not long enough to permit silica concentrations to drop to saturation. Therefore, at the injection wellhead, the spent brine remains supersaturated in silica and in addition contains about 200 ppm of suspended solids consisting primarily of silica and metal sulfides precipitated during the flash process. What needs to be done to produce an injectable brine is reasonably clear - namely separate and remove the suspended solids and produce a clarified brine that is not supersaturated in any solid species which would precipitate in the reservoir and impair injection longevity. The selection and design of such a process, however, is not clearcut and will require considerable experimentation with chemical additives, settling and separation processes, polishing steps, and related engineering operations.

Coagulants and Coagulant Aids^{9,10}

A preliminary, but integral step in removal of colloidal solids is the use of chemical coagulants and coagulant aids. The role of these additives is to 1) destabilize the colloids through neutralization of surface electrical charge. By lessening mutual repulsion forces, particles approach sufficiently close to allow attractive forces to become effective for particle agglomeration and 2) mechanical entrapment of particles into flocs that are more amenable to sedimentation processes.

The most commonly used coagulants are inorganic additives - iron salts, alum, and magnesium compounds. Organic polymers or polyelectrolytes are also

commonly used. Depending on their composition, they can be either anionic, cationic, or nonionic with variable charge density. Molecular weights can vary from less than a million in the case of primary polymeric coagulants to several million for polyelectrolytes used as flocculents or coagulant aids. Polymers adsorb and attach onto colloidal particles. This bridging action is an important factor in particle destabilization and aggregation. In a properly designed process, the selection of the chemical additive(s) and the amount used is crucial. Furthermore, the flocculation and sedimentation steps which follow are also critical. The goal is to provide the necessary environment for the particles to continue to agglomerate into larger and larger flocs to allow rapid and complete sedimentation, leaving a clear supernatant. Recirculation of the concentrate coupled with forced circulation of the liquid through the dense sediment is often helpful.

In general, the chemical additives have been developed primarily for removal of turbidity and colloidially dispersed solids from ambient temperature, low salinity waters that are commonly encountered in municipal water and sewage systems. Therefore, their stability and effectiveness in the higher temperature, high salinity Niland brines are virtually unknown and need to be investigated. Furthermore, it is not known whether these conventional additives are capable of functioning effectively with specifically amorphous silica colloids at the pH existing in the GLEF effluent.

Screening Tests of Chemical Additives

Experimental Procedure -

Spent brine was collected from the 10" diameter injection line near the Magmamax # 3 injection well and immediately transferred to 1000 ml beakers. The following test procedure was carried out using a Phipps & Bird ganged stirrer apparatus.

1. With mixer on at 100 rpm, chemicals are quickly added to each of 6 jars or beakers and mixed for 1 minute.
2. Mixer speed lowered to 40 rpm for 3 minutes.
3. Slow mixer to 10 rpm for 16 minutes.
4. Allow 10 minutes settling period before sampling supernatant and recording appearance of floc and clarity of supernatant.
5. Record initial and final temperature and pH, type and amount of additive

Chemical Additives Tested

Cationic, anionic, and nonionic polyelectrolytes and inorganic compounds such as FeCl_3 , alum, MgO , and $\text{Fe}_2(\text{SO}_4)_3$ were tested. The compounds were tested individually and in combination at different concentrations, pH, and

temperature. Time was also a factor taken into account since silica precipitation is a rate process.

The effectiveness of a particular additive is determined qualitatively and quantitatively. The qualitative factors include the rapidity of the floc formation, floc size and rate of growth, floc density or ability to rapidly settle, visual clarity of the supernatant, and the extent of post precipitation in the supernatant. Quantitative factors all involve the supernatant: Silica concentration, suspended solids concentration, and measured clarity.

The supernatant was filtered with a 1 μ m membrane filter to obtain residual suspended solids. Dissolved silica in the filtrate was determined by atomic absorption spectrophotometry. Although supernatant clarity was not measured in these tests it can easily be done with a conventional turbidity meter, or with a Spectrex Corp. laser particle counter which we have used with some success on Niland brines.

A constant temperature bath was also not yet available for those tests. Consequently, the brine cools from 85°C down to 55°C during the 30 minute test period. This should not adversely affect the performance of a coagulant, however. Clearly those additives which do show promise will require verification tests where cooling does not occur - conditions which more nearly correspond to the actual process.

Test Data and Results -

Table 3 lists the chemical additives tested, the concentrations used and test parameters.

Tests were performed with 6 jars simultaneously, one jar being the control. In the 70-80 jar tests conducted, the most notable feature was the amount and rapidity of floc formation in the control jar containing no additive. Apparently mixing significantly aids coagulation and agglomeration of solids. The addition of a polymer provides only slight improvement, mainly in ultimate size of the floc. Use of primary coagulants, alum and FeCl_3 help, but again only marginally. Polymers B-1185 or B-1190 at 2 ppm plus 20 ppm alum or FeCl_3 , and ZT-646 at 5 ppm produced the best results in normal pH ~5.5 brine, but again without significant improvement in floc characteristics over that of brine which contained no additive. In most instances, the supernatant contained appreciable cloudiness caused in part by post precipitation of silica and $\text{Fe}(\text{OH})_3$. The supernatant of the end of the 30 minute test period, still contained from 12-60 ppm solids $> 1 \mu\text{m}$. Post precipitation was not unexpected since none of these conventional additives were able to fully bring the silica concentration down to saturation from supersaturation levels. For pH 5.5 brine, it takes roughly 1.5-2 hours to allow the concentration of dissolved silica to drop to saturation. The rate can be greatly increased by raising the pH. When the pH of brine samples were raised to 5.9, the dissolved silica concentration dropped within 10 minutes to 150 ppm from supersaturated levels described above. Therefore, to eliminate silica post precipitation

TABLE 3. Chemical Additives Tested in Magmamax # 1 Spent Brine From GLEF

Test #	Polyelectrolyte	Type	Conc ppm	Inorganic	Conc ppm	Initial Temp °C	Final pH	Remarks
1-1	Control	-		-		85	5.5	
2	B-1100	Anionic	1	-		↓	5.5	
3	B-1130	↓	↓	-		↓	5.5	
4	B-1100			FeCl ₃	200	↓	2.8	
5	B-1130			FeCl ₃	20	↓	5.5	
6	B-1100	↓	↓	Alum	20	↓	5.5	
1-2	Control	-		-		85	5.2	
2	B-1175	Cationic	2	-		↓	↓	
3	B-1180	↓	↓	-		↓	↓	
4	B-1185			-		↓	↓	
5	B-1190			-		↓	↓	
6	B-Poly Floc 3	Nonionic	20	-		↓	↓	
1-3	Control	-				82	5.1	
2	B-1175	Cationic	2	FeCl ₃	20	↓	↓	
3	B-1180	↓	↓	↓	↓	↓	↓	
4	B-1185					↓	↓	
5	B-1190					↓	↓	
6	B-Poly Floc 3	Nonionic	20	↓	↓	↓	↓	
1-4	Control	-				80	4.9	
2	B-1175	Cationic	10	-		↓	↓	
3	B-1180	↓	↓	-		↓	↓	
4	B-1185			-		↓	↓	
5	B-1190			-		↓	↓	
6	B-Poly Floc 3	Nonionic	20	-		↓	↓	
1-5	Control	-				81	5.3	
2	B-1175	Cationic	20	-		↓	↓	
3	B-1180	↓	↓	-		↓	↓	
4	B-1185			-		↓	↓	
5	B-1190			-		↓	↓	
6	B-Poly Floc 3	Nonionic	↓	-		↓	↓	
1-6	Control	-				39	5.5	Pre-test
2	B-1185	Cationic	2	-		↓	5.5	1.5 hr.
3	B-1185	Cationic	↓	FeCl ₃	20	↓	5.3	retention
4	B-1130	Anionic		-		↓	5.4	plus
5	B-1130	Anionic		FeCl ₃	20	↓	5.3	cooling
6	-		↓	FeCl ₃	20	↓	5.2	

TABLE 3. Chemical Additives Tested in Magmamax # 1 Spent Brine From GLEF - Continued -

Test #	Polyelectrolyte	Type	Conc ppm	Inorganic	Conc ppm	Initial Temp °C	Final pH	Remarks
1-7	Control					81	5.3	Pre-test
2	B-1185	Cationic	2	-		↓	5.3	1.5 hr
3	B-1185	C	↓	FeCl ₃	20	↓	5.1	retention
4	B-1130	Anionic		-			5.3	@
5	B-1130	A		FeCl ₃	20		5.1	81°C
6	-		↓	FeCl ₃	20	↓	5.1	
1-8	Control					84	5.4	
2	B-1185	Cationic	2	FeCl ₃	20	↓	6.1	NaOH added
3	-			FeCl ₃	↓	↓	6.1	NaOH added
4	B-1185	C	2	Alum			4.4	HCl added
5	B-1185	↓	↓	Alum			5.4	
6	B-1185	↓	↓	Alum	↓	↓	6.0	NaOH added
1-9	Control					84	5.5	
2	-			MgO	50	↓	5.8	
3	-			Fe ₂ (SO ₄) ₃	20	↓	5.4	
4	B-1130	Anionic	5	-			5.5	
5	DC Z-6070	Silicone	50	-			↓	
6	UC A-1100	Silicone	50	-		↓	↓	
1-10	Control					86	5.1	
2	ZT-646	Anionic	5	MgO	50	↓	5.4	
3	↓	↓	↓	↓	100	↓	5.6	
4					200		5.8	
5					300		6.0	
6					500	↓	6.1	
1-11	Control					87	5.2	
2	-			NaOH	150	↓	5.8	
3	-			MgO	500		6.1	
4	ZT-646	Anionic	5	MgO	500		6.3	
5				-			5.3	
6				NaOH	150	↓	5.9	

Table Notes: B = Betz
 DC = Dow Corning
 UC = Union Carbide
 ZT = Zimmite
 ZT 628, 636, 644, 651 also tested up to 20 ppm by company representative. ZT-646 produced best results.

sufficient time must be allowed for monomeric silica to polymerize to the point where supersaturation no longer exists in the brine after sedimentation. Raising the pH can shorten this time significantly, but at some expense, namely increased $\text{Fe}(\text{OH})_3$ precipitation.

There is some indication from the jar tests that in the absence of post precipitation, coagulation followed by sedimentation leaves a supernatant solution which is relatively free of suspended solids. In tests 4-1 and 4-8 where the pH was 2.8 and 4.4, respectively, the supernatant was clear and in test 4-8 contained only 3.8 ppm suspended solids $> 1 \mu\text{m}$. Elimination of post precipitation is clearly desirable, and retaining the brine for 1.5 hours can achieve this. In addition, there was some expectation that aging the brine would improve solids aggregation and flocculation; however, no improvement was noted. Finally, retention with cooling to 39°C before addition of a polymer to minimize thermal degradation of the polymer, if any, also did not help.

Raising the brine pH to 5.9 with NaOH not only rapidly lowered silica concentration, but also produced large floc particles (.2-.3mm) that settled reasonably well. We did not observe any additional benefit through combined use of polymers and/or inorganic coagulants at pH 5.9 - 6.1. However, these tests were few in number and not conclusive.

Magnesium oxide, MgO , known to be an adsorbent for dissolved silica, was added at concentrations of 50, 100, 200, 300, and 500 ppm. Good flocs were produced, particularly at the higher concentrations of MgO where the brine pH was also elevated. The resultant supernatant solutions were not

analyzed for residual silica, however.

These tests have provided significant insight into the benefits and limitations of chemical additives in coagulating and flocculating colloidal solids in spent geothermal brines. Although these kinds of tests will continue, sufficient data have been obtained to begin tests with pilot-sized process equipment. On site, we plan to test a thickener-clarifier with sludge recirculation. A rotary vacuum precoat filter will be tested as a means of dewatering the sludge. Tests of precoat pressure filters and mixed media sand filters are planned to determine their effectiveness in polishing the overflow stream from the clarifier.

SUMMARY

- Control Samples (pH ~5.5, Temp 85°C), without additive
 - Agitation significantly aids coagulation and flocculation of colloidal solids in spent geothermal brines.
- Effect of Temperature
 - Temperature in the range of 40°C to 85°C does not appear to benefit or impair the effectiveness of a coagulant.
- Post precipitation
 - At brine pH of 5.5 without aging, supernatants remain supersaturated, and cloud with silica post precipitation. Coagulants do not help to increase the rate of removal of dissolved silica.
- Effect of Aging
 - Retention of brine for 1.5 hours reduces silica concentration to saturation levels, but does not improve ultimate floc characteristics.

- Effect of pH

- Elevating the brine pH to 5.9 drops silica concentration within 10 minutes to saturation levels and rapidly produces a floc of good consistency for sedimentation. Supernatant clouds with $\text{Fe}(\text{OH})_3$ post precipitation.

- Polyelectrolytes

- Cationic and anionic polymers are slightly beneficial.

- Inorganic coagulants

- Alum, FeCl_3 , $\text{Fe}_2(\text{SO}_4)_3$, and MgO are slightly beneficial. More effective with pH rise.

- Supernatant clarity

- In the absence of post precipitation, coagulation with settling results in a supernatant that is relatively free of suspended solids > $1\mu\text{m}$.

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