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SAMPLING PROCEDURE FOR ATMOSPHERIC GEOTHERMAL BRINES

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ABSTRACT

Thermodynamic and chemical changes can alter the characteristics of geothermal brine samples significantly. A procedure which minimizes these changes has been developed for sampling atmospheric geothermal brines. The method is fast with minimal cooling and yields representative samples which have been stabilized to preserve their integrity. The procedure provides reliable suspended solids data and both the solid and liquid samples are suitable for elemental analysis. The procedure is also a valuable tool to aid in monitoring a geothermal brine conditioning system. Data are included from a flow test at an MCR Geothermal well in the Imperial Valley area of California to illustrate the utility of the sampling procedure.

INTRODUCTION

In any geothermal sampling procedure certain factors must be considered in order to assure representative samples, i.e. thermodynamic and chemical instability are inherent in many geothermal systems and steps must be taken to minimize the effects of these instabilities. The procedure described here is successful at minimizing these effects and yields samples of high integrity.

Many sampling procedures have been used to monitor components of geothermal brines. While having similarities to methods described by Hill and Otto, 1977, and Kindle, 1980, this procedure was designed primarily to aid in monitoring suspended solids and dissolved silica levels in flashed (atmospheric) geothermal brines. This sampling procedure is a practical method based on field experience.

Once the sample of the geothermal fluid is stabilized, it is then possible to obtain a complete chemical profile of the brine.

The information obtained from the samples taken by this procedure is valu-

able in that it allows a complete brine conditioning system to be monitored. Reliable data are necessary to operate such a system smoothly and efficiently.

APPARATUS

Careful consideration was given to the selection of the sampling apparatus. The equipment must be heat resistant, durable, and non-corrosive. Silica based glass should be avoided. Not only does the glass provide a surface for possible silica precipitation but the silica in the glass is also minutely soluble in the brine sample (Franson, 1976). Kindle, 1980, recommends the use of high purity acid for pH modification to minimize the introduction of additional elements.

Below is a list of the equipment used in the sampling procedure:

Sample Collection

1. one liter insulated polypropylene beaker
2. 50 cc disposable polypropylene syringe
3. -10 to 260°C thermometer (1° subdivisions)
4. insulated gloves

Sample Filtration and Stabilization

1. Millipore filtering apparatus (47 mm)
2. 0.45 micron acetate filters (47 mm)
3. one liter polypropylene vacuum flask
4. vacuum tubing, vacuum pump, and cold trap
5. distilled water
6. reagent hydrochloric acid
7. 250 ml polypropylene graduated cylinder

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Sample Preservation

1. 250 ml polypropylene sample bottles
2. tight-seal polystyrene petri dishes

PROCEDURE

Two operational criteria must be met before sampling atmospheric geothermal fluids: a) Brine characteristics can change considerably during well start-up. For this reason a good practice is to allow 24 hours of well flow before beginning sample collection (Kindle, 1980). b) In a continuous system "steady state" conditions should be approximated to ensure more representative samples.

Sample Collection

A well designed brine treatment system will have sample ports at various locations within it. These sample ports should consist of a ball valve and retractable probe. The probe can be inserted into the mainstream of the brine flow for a homogeneous, representative sample (Kindle, 1980).

Time and temperature are factors of critical importance in the precipitation of brine solids. For this reason, expedient sample collection and preparation will minimize temperature loss and subsequent solids precipitation (Hill et al., 1979). It is good practice to rinse the collection container with hot brine before taking the actual sample. This serves to preheat both the collection container and the sample port as well as to flush the probe. In this sampling procedure, one liter of brine is collected into the polypropylene beaker. The temperature of the brine is immediately recorded. From this one-liter portion a quantity of 50 mls is extracted for filtration.

Sample Filtration and Stabilization

Stabilization of the brine filtrate is necessary to preserve sample integrity. A five-fold dilution of the filtrate with distilled water is sufficient to minimize silica precipitation (Iler, 1979). Iler also states that the kinetics of silica precipitation are slowed by acidification of the filtrate to pH 2.0. Iron solubility is also maintained at pH 2.0 (Hill and Otto, 1977). To determine the amount of acid necessary to adjust the pH of the diluted filtrate to 2.0 a titration must be done. 200 ml portions of distilled water are acidified in advance for use in sample stabilization.

The filtration/stabilization process is as follows:

1. place 200 mls of acidified water into the filtration flask
2. place preweighed 0.45 micron Millipore filter into filtering apparatus
3. rinse 50 ml syringe with brine
4. extract a 50 ml portion of the brine from the one liter sample
5. filter the 50 ml portion*

Depending of the level of suspended solids in the brine sample, a sample size other than 50 ml may be desirable. The actual filtration of the sample should be fast and the presence of large amounts of suspended solids in the brine could cause a 50 ml sample to filter too slowly.

Sample Preservation

The diluted and acidified filtrate should be stored in a 250 ml sample bottle. The filter cake should be rinsed with 100 ml of distilled water and stored in a tight-seal petri dish.

Both the filtrate and filter cake are suitable for storage and later analysis. The washed filter cake can be dried and weighed for suspended solids determination and with digestion, elemental analysis can be done. The filtrate and filter cake will give reliable, reproducible values for soluble and suspended silica, respectively, for any atmospheric brine sample prepared using this procedure.

ANALYSIS

Of primary importance to our studies was the analysis of the filtrate and filter cake for silica. We have defined soluble silica to be any silica which passes through a 0.45 micron filter. This includes some polymeric silica (Iler, 1979). Four methods are available for soluble silica determination: a) molybdate method b) atomic absorption (AA) c) heteropoly blue method d) inductively coupled plasma (ICP). Of these methods ICP and heteropoly blue were the most useful for our purposes. The molybdate method proved to be of limited use because of iron-complex interference. The AA method exhibited limited sensitivity on the dilute filtrate samples. Because of the expense of ICP analysis, the

* Vacuum filtration may cause instantaneous precipitation of solids; at this time this effect is thought to be minimal. Further testwork in this regard is warranted.

heteropoly blue method was used (Franson, 1976). The method is fast, reproducible, and reliable. The suspended solids values are determined by drying the filter cake at 110°C and weighing (Hill and Otto, 1977). The cake is then digested for elemental analysis.

FIELD DEMONSTRATION

A field demonstration of the sampling procedure was performed at a 30-day flow test at an MCR Geothermal well in South Brawley, California. The brine conditioning system used during the test is shown in Figure 1. Table 1 shows suspended solids and soluble silica data for several series of samples from the conditioning system. The reproducibility of this data was very acceptable; 6% variance for the suspended solids and 1% for the dissolved silica analysis.

The suspended solids data are useful for the determination of the clarification and filtration performance of the system. The first and second sets of suspended solids data clearly illustrate effective solids increase through the fluidized beds (Figure 1). This solids increase is desirable in brine clarification (Featherstone, 1979). The first five data sets show a decrease of suspended solids through the settling tanks as would be expected. The sixth set indicates that the settling tanks were undergoing sludge carry-over, demonstrated by an unusually high level of suspended solids in the effluent. This might indicate that the sludge levels in the settling tanks are too high and that sludge removal may be required. Sets three and five show that the suspended solids levels increase through surge tank No. 2 prior to reinjection. Monitoring suspended solids levels in the reinjection fluid is critical for the protection of the reinjection zone (Jorda, 1978).

The soluble silica in all instances, shows a decrease through the system. The precipitation of silica occurs as a function of time and temperature. These data, used in conjunction with kinetics data on silica precipitation, can be useful in determining silica equilibrium values in the system. Thus it is possible to predict how much silica will have precipitated at any given position in the conditioning system.

Table II gives the results of ICP analysis of the suspended solids of sample set No. 5. From a data set such as this, it is possible to monitor component changes in the brine as it is processed by the system.

CONCLUSIONS

A sampling procedure for atmospheric

geothermal brines must satisfy two requirements to be effective. First, the procedure must minimize the thermodynamic and chemical changes that are inherent to the collection of samples of geothermal fluids. Second, the procedure must yield a sample that remains chemically stable until analyzed.

The sampling procedure as described provides a means for satisfying these requirements. It provides a reliable method for determining the amount of suspended solids present at any point in a brine conditioning system. It also provides a method for stabilizing a filtered brine sample for quantitative and qualitative component analysis. With these requirements satisfied, an accurate representation of the brine as it existed when taken from a given sampling location can be obtained. Finally, this sampling procedure enables its user to accurately monitor a geothermal brine conditioning system.

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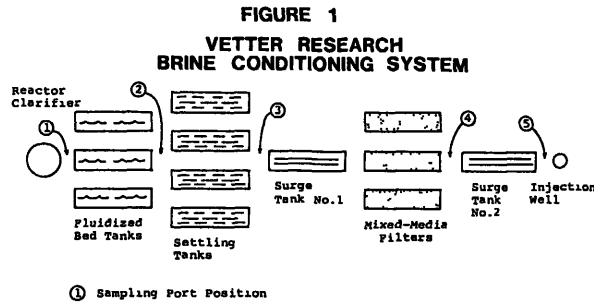


TABLE I
SYSTEM ANALYSIS SAMPLES

Set No.	Sample No.	Flow Rate bbi/day	Sampling Position *	Temperature (°C)	Suspended Solids (mg/L)	Soluble SiO ₂ (ppm)
1.	12-10-1	14,000	1	95.0	624	242
	12-10-2D		2	92.5	656	212
	12-10-3		3	79.0	330	181
2.	12-10-4	14,000	1	98.0	590	272
	12-10-5		2	90.5	638	227
	12-10-6		3	84.0	368	189
3.	12-11-7	11,000	1	97.0	604	256
	12-11-8		2	84.5	406	194
	12-11-9		3	85.0	184	186
	12-11-10		4	79.0	46	155
	12-11-11		5	75.0	122	153
4.	12-11-12	11,000	1	97.0	642	257
	12-11-13		2	91.5	628	220
	12-11-14		3	82.0	308	180
	12-11-15D		4	74.0	148	147
	12-11-16		5	70.0	136	141
5.	12-13-16	26,000	1	98.0	600	276
	12-13-17		2	96.0	546	221
	12-13-18		3	89.0	434	181
	12-13-19		4	83.0	222	149
	12-13-20		5	79.0	240	146
6.	12-14-1	25,000	1	97.5	584	286
	12-14-2		2	97.0	660	244
	12-14-3		3	91.0	1076	180
	12-14-4		4	79.0	744	151
	12-14-5		5	80.5	740	142

* Refer to Figure No. 1

** Soluble silica determined by heteropoly blue method

TABLE II
ICP ANALYSIS - SET NO. 5 SUSPENDED SOLIDS

Constituent	12-13-16		12-13-17		12-13-18		12-13-19		12-13-20	
	(%)	(mg/L)	(%)	(mg/L)	(%)	(mg/L)	(%)	(mg/L)	(%)	(mg/L)
Total Suspended Solids	100.0	600.0	100.0	546.0	100.0	434.0	100.0	222.0	100.0	240.0
Silica (as SiO ₂)	60.0	360.0	60.5	330.3	51.8	224.8	65.8	146.1	52.3	125.5
Iron	17.1	102.6	17.1	93.4	15.9	69.0	21.3	47.3	18.7	44.9
Sodium	1.9	11.4	1.6	8.7	2.8	12.1	1.5	3.3	4.7	11.3
Lead	.8	4.8	.9	4.9	.6	2.6	.4	.9	.4	1.0
Potassium	.4	2.4	.3	1.6	.4	1.7	.2	.4	.5	1.2
Copper	.2	1.2	.2	1.1	.1	.4	.1	.2	.1	.2
Manganese	.2	1.2	.2	1.1	.2	.9	.1	.2	.2	.5
Boron	.2	1.2	.1	.5	.1	.4	.1	.2	.1	.2

Note: This is only a list of the major constituents