Simulated Down-hole Casing Corrosion Protection Tests by Addition of Filming Amine Products into Geothermal Injectate at The Geysers

Allen Sonneville, Brian Benn, and Tim Conant

Calpine Geysers Power Plant, Middletown, CA

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ABSTRACT

Proprietary filming amine chemicals were tested for efficacy and economic dose rate in a test apparatus simulating injection well down-hole temperature and corrosivity conditions. The results of the test were used to select the most economical corrosion protection injection additive and to determine the effective dose rate required. This paper describes the reasons for utilizing a test skid that simulates down-hole conditions and presents the results and conclusions of the filming amine injection testing.

Background

Down-hole casing corrosion in geothermal injection wells can result in the loss of injectivety requiring millions of dollars in drilling costs to repair or replace an injection well. Most injection wells at The Geysers are lined with mild steel casing which is susceptible to corrosion attack especially from corrosive injectate water under down-hole temperature conditions. For more than a decade at The Geysers corrosion protection for mild steel lined injectors has been provided by adding filming amine chemicals at the injection wellhead. Traditional product dosing for corrosion control utilizes corrators and corrosion coupons installed in the surface injectate supply piping to measure corrosion rate and thereby determine the amine dosage rates needed to protect the injector casing (Figure 1).

Unfortunately, monitoring corrosion in this manner does not provide data representative of the in situ conditions at depth in the injection well; and the efficacy of the protective amine can only be determined by down-hole caliper measurements, which determine casing wall thinning. If damage occurred due to insufficient inhibitor, it's already too late to adjust your inhibitor addition rate. Two notable examples of the failure of surface corrosion monitoring and dosage determination are as follows:

1. The Barrows 7 injector failed due to pitting corrosion from oxygen attack despite continuous corrosion inhibitor additions to the injection water (Figure 2).

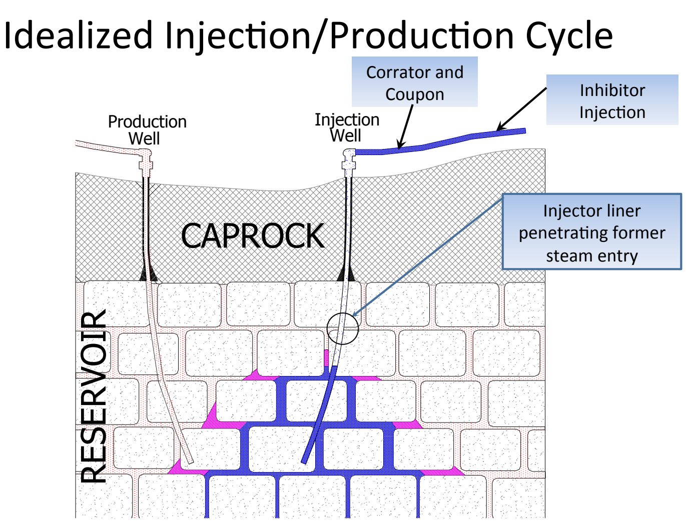


Figure 1. Idealized injection/production cycle.

Figure 2. Barrows 7 Injection Liner Oxygen Pitting Corrosion.

Traditional corrosion monitoring methods, (corrators and corrosion coupons) were being utilized to determine the dose rate and effectiveness of the inhibitor applied. This continuous corrosion monitoring was restricted to the surface piping upstream of the injection well after amine addition.

2. Acidic injectate in CMHC2 from a Burner H_2S abatement equipped plant resulted in >50% wall loss over a one year period. See well caliper log (Figure 3).

In both cases the injection well casing corrosion occurred where the injection liner had penetrated a former steam entry (Figure 4).

Heating of the exterior of the casing results in loss of the filming amine barrier and accelerated corrosion attack. In the case of Barrows 7, relatively cool oxygen saturated injectate water falling from the surface into the injection well was heated in the steam entry zone, causing the accompanying pitting corrosion (Figure 2). Although filming amine corrosion inhibitor accompanied the injectate water, and surface corrosion monitoring indicated that inhibitor dosing was adequate, the heat resulting from former steam entries on the outside of the injection casing defeated the protective amine film on the pipe wall and allowed corrosion to proceed. Similarly, at CMHC2, generalized corrosion occurred in the heated zone when acidic injectate corrosion was accelerated in the heated area. pH drop due to chemical and biological aging of injectate water from a Burner H_2S abatement equipped plant can result in acidic water with a pH of 2.5. This low pH can neutralize the amine portion of the inhibitor and result in generalized corrosion of the casing, unless the neutralized inhibitor is continuously replaced with fresh inhibitor. Injectate water at The Geysers falls under vacuum from the surface, which can result in scouring off of the filming amine inhibitor at depth as the directional change occurs in the well. Again, the remedy is to continuously replace the amine layer by adequate dosing.

The remedy in the case of Barrows 7 and other injection wells was to double the inhibitor dosage rate and run calipers to determine if the dosage was adequate. This was not only expensive but it did not solve the problem of determining the most effective and economical dosage rate. To that end, Calpine constructed a test skid to simulate down-hole injection conditions, and determine dose rate and efficacy of inhibitor products.

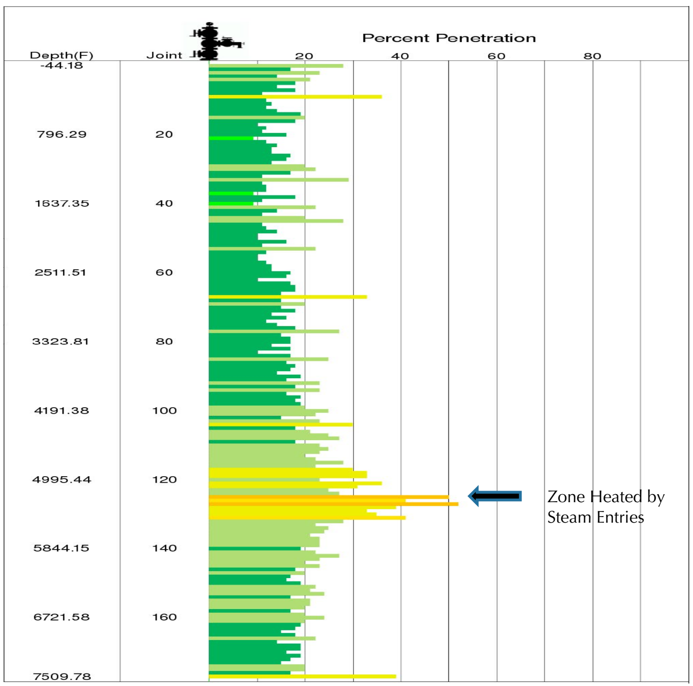


Figure 3. Generalized Corrosion from Acidic Injectate: CMHC Casing Penetration vs Depth.

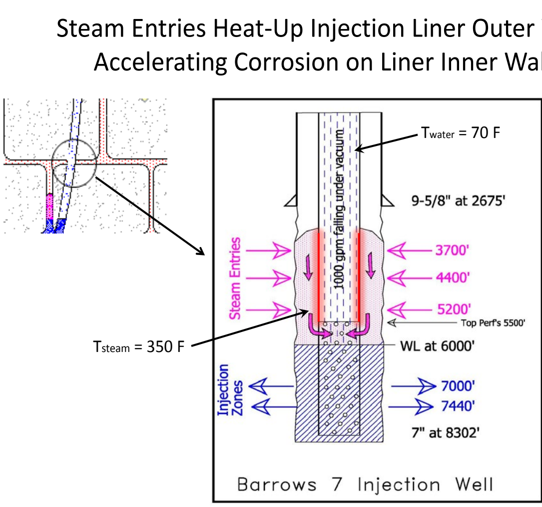


Figure 4. Injectate dissolved O_2 attacks unprotected casing.

Test Skid Design

The skid consists of four parallel runs of two vertically oriented single pass shell and tube heat exchangers. Injectate water is passed "tube side" through pre-weighed pipe nipples which act

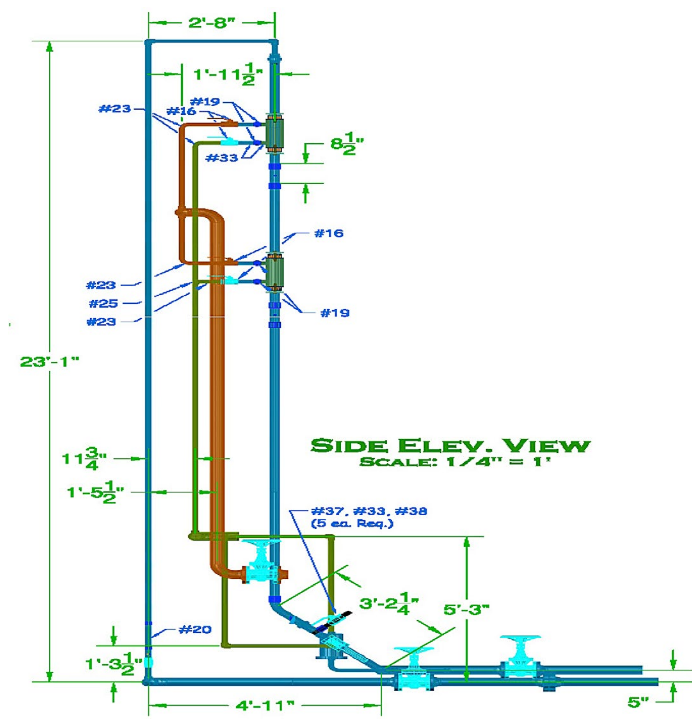


Figure 5.

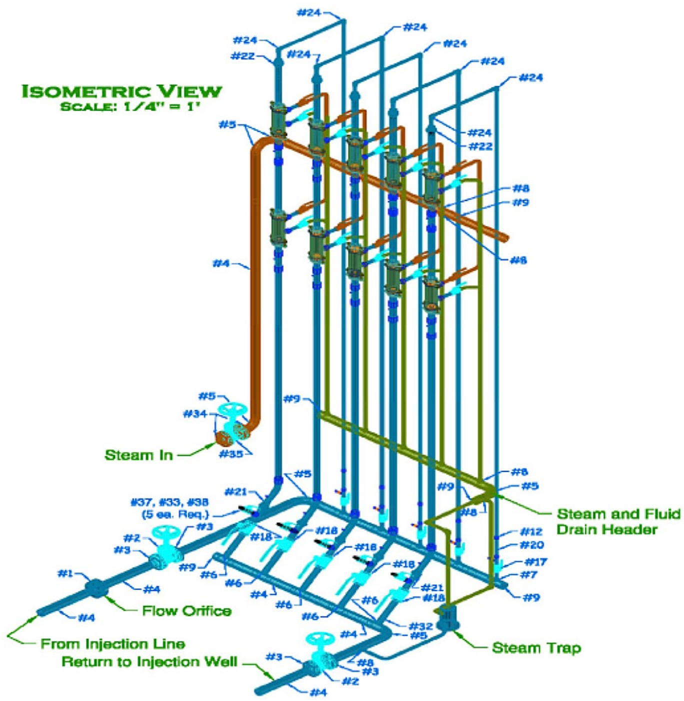


Figure 6.

as a corrosion "coupons". Steam is added "shell side" to heat the outer wall of the pipe nipple/coupon thus simulating an injection casing penetrating a former steam entry in the reservoir. Corrosion inhibitor (filming amine) is added to the injectate water before passing through a static mixer which ensures adequate mixing as it rises 23 feet to the top of the test loop. At the top of the skid just when the water starts to fall, a specifically designed nozzle is located to throw the water towards the pipe wall for a more uniform treatment. Injectate corrosivity is measured with a corrator and a traditional in situ corrosion coupon as the heated water leaves the bottom of the skid. As shown on the side view schematic (Figure 5), two steam jackets are located in line on each test loop to raise the surface temperature of the pipe wall and to elevate water temperatures by several degrees.

Two of the pipe nipple coupons are located below each of the steam jacket and a third long curving pipe nipple coupon is located at the bottom of the test loop. The pipe nipple sections inside the steam jackets can also serve as coupons and be evaluated for corrosion. A corrator probe measures the relative corrosion rate at the outlet of each test loop to provide real time indication on the treatment effectiveness for dosage adjustments. Also on the outlet is a temperature sensor for each test loop to give indication of a corrosion breach inside the steam jackets where steam can flow into the testing solutions. When steam breaks through the temperature rises dramatically. The waters of each test loop are then recombined and returned to the injection well downstream of the well's flow control valve. Since the injection well is on vacuum those same pressures are propagated to the downward leg of the test loop simulating down-hole conditions.

The test skid can be disassembled and relocated to any injection well. The skid requires a stream of about 200 gpm injectate water to be diverted from the well to the test skid. The amount of water put through the skid is measured by an orifice plate flow meter and distributed equally to the five test loops (see Figure 6 isometric). Multiple test loops enables several different treatments to be evaluated at the same time.

Results

To date two successful trials have been completed on the test skid. The first trial was a screening of proprietary filming amine products from four different chemical suppliers in which the amine that performed the best in terms of effectiveness and cost would be selected as the primary Geysers supplier. The test skid was placed at the McCabe 5&6 injection well GDC 32A13 with a slip stream of water to the test skid of 200 to 350 gpm to provide 40 to 70 gpm per test loop. The chemical suppliers set and controlled dosage rates. Evaluation of the corrosion coupons was performed by both Calpine Geysers Chemistry Lab and *Structural Integrity Incorporated*, an internationally known corrosion measurement company. The pipe nipple coupons were all acid cleaned and the

Photo 1a and 1b. Corrosion Coupon Pipe Nipple Sliced Lengthwise.

Table 1. Test #1 results.

		Initial Weight grams	Final Weight grams	Surface Area in^2	Test Duration Days	Total Corrosion Rate mills per year	Average Corrosion Rate mills per year
Untreated Control	1B	698.38	661.40	38.33	50	55	58
	1A	701.63	665.60	38.33	50	54	
	1	2678.76	2516.20	144.37	50	64	
Supplier#1	2B	694.19	677.00	38.33	50	26	31
	2A	674.86	657.20	38.33	50	26	
	2	2686.82	2583.78	144.37	50	41	
Supplier#2	3B	680.10	659.00	38.33	50	31	35
	3A	700.01	685.00	38.33	50	22	
	3	2654.76	2523.72	144.37	50	52	
Supplier#3	4B	681.07	658.50	38.33	50	34	36
	4A	695.89	679.00	38.33	50	25	
	4	2667.15	2539.33	144.37	50	50	
Supplier#4	5B	690.22	677.10	38.33	50	20	30
	5A	697.06	688.70	38.33	50	12	
	5	2645.85	2502.01	144.37	50	57	

long curved coupons were lightly bead blasted before acid cleaning. The results of that trial can be found in Table 1. (The names of the suppliers have been withheld). An example of one of the corrosion coupon pipe nipples is shown in Photo 1.

The untreated control test loop had the highest corrosion rates and showed pitting in the pipe section inside the steam jackets. All of the amine treated loops showed less corrosion than the control. The long curved coupons were more difficult to evaluate due to the length and curvature making bead blasting difficult and due to exterior corrosion caused by the ambient environment at The Geysers. This external pipe corrosion affected the weight loss after cleaning and inflated the corrosion rate. Regardless of whether those curved coupons are included in the average calculation, the product from Supplier #4 performed the best with Supplier #1 a close second. The difference in corrosion rates among Suppliers on average was not large, so the treatment cost differentiated the winners. The test skid results enabled the Geysers to select treatment suppliers not only on performance but cost as well, resulting in a savings of approximately 50% compared to previous the Geysers filming amine treatment cost.

Trial #2

The treatment goal of the second test skid trial was to determine the least cost alternative that achieves corrosion rates of less than 10 mills per year (mpy). In previous trials the corrosion rates of the amine treatments were greater than this target, ranging from 12 to 57 mills per year (mpy), so a different approach to inhibition was tried. It was hypothesized that bacteria (sulfate reducing bacteria) play a role in the corrosion process enhanced by the presence of waste water. This test entailed adding filming amine in conjunction with a biocide. The two best performing amines from the previous trial, Nalco and US Waters, whom were now supplying our filming amine inhibitor products, were selected to participate in this trial with the vendors deciding on which biocide was best suited and compatible with their product. (Nalco modified their amine product for the Geysers to reduce product flammability). Their new product was labeled TX-15472, but was essentially the same active chemical used in the previous trial and already in use at The Geysers.

Treatment

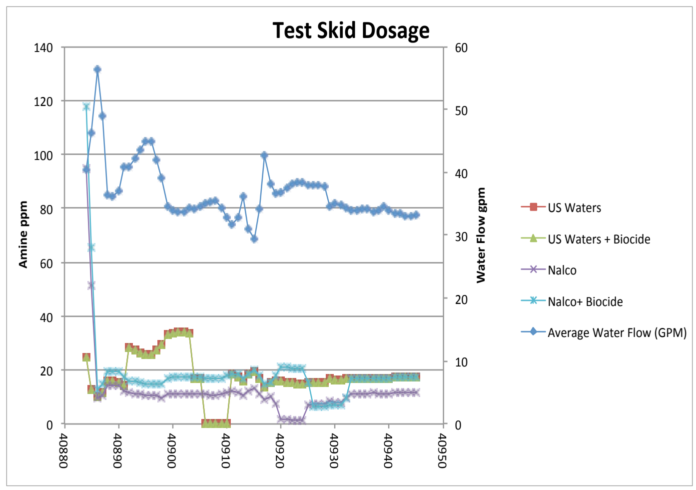
The two vendors selected different biocides and different treatment regimes. US Waters added DBNPA (Dibromonitrilopropionamide) on a continuous basis (3 ppm) while Nalco added a Quaternary amine (the same biocide is used in the Geysers Unit 17 cooling tower) on a daily batch at a dosage of 42 ppm. The treatment programs were as shown in Table 2.

Table 2. Trial #2 treatment programs.

	Vendor	Treatment	Amine ppm	Biocide ppm
Test Loop 1	Control	None		
Test Loop 2	US Waters	GWT4DF	17.5	0
Test Loop 3	US Waters	GWT4DF + DBNPA	17.5	3
Test Loop 4	Nalco	TX-15472	12	0
Test Loop 5	Nalco	TX-15472 + Quat (90005)	16	42

Test Skid Trial #2 started on 12/7/11 and ended on 2/7/12 for a total of 61 days. On the first day of the trial the vendors were given 24 hours to passivate their test loop sections before steam was added to the steam jackets. In future test skid trials this passivation period will be eliminated since the corraters have shown passivity occurs relatively quickly dropping from the initial 100 mpy to less than 10 mpy within hours of amine addition. The different doses of amine in the two Nalco test loops were unintentional. The pumps were initially set with identical frequency and stroke, but test loop #4 pumped less volume. US Waters increased amine addition for 12 days when elevated corrator readings called for increasing their average amine dosage by two ppm.

The trial was relatively trouble free in terms of chemical feed. The most notable upset was a short duration pumping failure on three of the four treated test loops (see Test Skid Dosage graph). When the upsets did occur the corrators registered no increase in corrosion rates with the lack of amine addition. This indicates that filming amine is quite resilient and will stick to the pipe walls through minor interruptions of feed. The dosages of each treatment are shown in Graph 1:



Graph 1.

Trial #2 Results

Water through the test skid was shut off on 2/6/12 and chemical feeds terminated due to a field injection problem. The test skid was dismantled on 2/7/12. George Licina from "Structural Integrity" and both amine Suppliers were present for the dismantling. Structural Integrity was present to quantify biological activity in test loop sections using a field kit measuring the following from each of the upper 6 inch pipe coupons:

- Low nutrient bacteria
- Iron bacteria
- Anaerobes
- Acid Producing bacteria
- Sulfate reducing bacteria (SRB)

The top 6 inch pipe sections were then shipped to Structural Integrity to determine the weight of the pipe after removing the internal deposits, analyze the internal deposits to determine composition and cross-section each corrosion coupon to document any corrosion or metal wastage along the internal surface. The rest of the coupons were cleaned and weighed in the Calpine Geysers Lab.

Injectate water chemistry varied throughout the trial with more wastewater present during the first half of the trial as determined by phosphate concentrations (Table 3).

Table 3. McCabe Injection Water.

Date	12/15/11	12/21/11	12/29/11	1/11/12	1/24/12	2/2/12	
pH	7	6.9	6.9	6.9	6.6	6.9	
Alkalinity	100	90	110		80	67	mg/l as CaCO3
Conductivity	2200	2000	1800	2200	3200	2500	Umhos/cm
Cl	34	42	35	39	7.3	12	mg/l
NO2-N	1	1	0.3	ND	ND	ND	mg/l
S2O3	76	100	92	23	7	103	mg/l
NO3-N	0.7	1	2.7	ND	ND	ND	mg/l
PO4	2	3.2	3.8	4.5	0.3	0.5	mg/l
SO4	630	526	486	625	898	840	mg/l
Na			34				mg/l
NH4							mg/l
K			4				mg/l
Mg			3				mg/l
Ca			12				mg/l

The corrosion rates for all treatments were remarkably similar with no apparent affect from biocides (Table 4). No significant difference was detected between the effectiveness of the Nalco and US Waters filming amines.

The corrosion rate in the control was only 34 mpy compared to 58 mpy in the previous trial at the same location. It is unclear why corrosion rates were so much different, but may be attributed to either time of year or water chemistry. The water temperature leaving the skid was an average of five degrees warmer this year and significantly more waste water was added to the mix the first half of this year's testing. The pipe section located in the uppermost steam jackets had notably less oxygen attack this year compared to last as measured by the pitting at the heated zones. It is possible oxygen concentrations were lower due to greater biological activity consuming the oxygen.

The average corrosion rates in all the amine treatments met or exceeded the 10 mpy goal. The coupons in the heat exchangers had the highest corrosion rates as expected. The treated samples showed little sign of microbiologically induced corrosion (MIC). According to Structural Integrity there is a definite MIC influence from SRB attack in the control sample. In general SRB's are abundant in all the pipe coupons, but only influenced corrosion in the control where an amine protective layer was absent. Details of the biological results are available in the Structural Integrity Report.

Table 4.

		Initial Weight grams	Final Weight grams	Area in^2	Days	Total Corrosion Rate mpy	Average Corrosion Rate mpy
Nalco + Quat Biocide	1B middle	1078.72	1077.6	36	61	1.45	
Nalco + Quat Biocide	1C top	1074.8	1067.9	36	61	8.94	
Nalco + Quat Biocide	1D curved	2661.79	2651.3	135	61	3.61	
Nalco + Quat Biocide	top exchanger	4767	4721.6	155	61	13.62	6.9
Nalco	2B	1029.92	1028.8	36	61	1.45	
Nalco	2C	1076.17	1069.4	36	61	8.77	
Nalco	2D	2680.93	2672.9	135	61	2.76	
Nalco	top exchanger	4821.48	4785.16	155	61	10.89	6.0
US Waters+ DBNPA Biocide	3B	1028.85	1027.7	36	61	1.49	
US Waters+ DBNPA Biocide	3C	1064.61	1056.8	36	61	10.12	
US Waters+ DBNPA Biocide	3D	2676.75	2664.1	135	61	4.35	
US Waters+ DBNPA Biocide	top exchanger	4785.16	4739.76	155	61	13.62	7.4
US Waters	4B	1052.7	1051.6	36	61	1.42	
US Waters	4C	1047.46	1040.8	36	61	8.63	
US Waters	4D	2674.98	2661.7	135	61	4.57	
US Waters	top exchanger	4776.08	4721.6	155	61	16.34	7.7
Control Middle	5B	1078.56	1052.9	36	61	33.24	
Control Top	5C	971.09	944.8	36	61	34.05	
Control Bottom	5D	2670.08	2575.7	135	61	32.45	
Control	top exchanger	4830.56	4703.44	155	61	38.13	34.5

Treatment Costs

There was no significant difference between the treatment cost and effectiveness between US Waters amine GWT4DF and Nalco's amine TX-15472. Both products are currently in use at The Geysers.

Conclusions

Surface measurements of injectate corrosivity cannot be trusted to give an accurate picture of the corrosion rate down-hole in an injection well. Dosage and efficacy can be determined by testing the inhibitor products by in-situ simulated conditions.

Filming amine corrosion inhibitor adequately provides protection for corrosive conditions encountered due to injection casing heating that occurs when an injection well penetrates a former steam entry.

Test skid trial #2 indicated no benefit from biocide addition when added in conjunction with filming amine. The filming amines seem to afford ample protection from corrosion in the heated zone, while the control showed significant corrosion influenced by SRB's. It is still possible that a biocide could be added in replacement of an amine to control corrosion as long as oxygen is minimized. When amines are added no biocide is necessary.

References

Figure 1 and Figure 4: Joe Beall, Presentation "The Geysers Geothermal Field" November 2, 2010.

Structural Integrity Associates, Inc. Test Report "Analysis of Corrosion Coupons from the Geysers Geothermal Power Pant" Ref: Project # 1200161.00.