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Geysers Power Plant H₂S Abatement Update

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ABSTRACT

H₂S emissions were a major obstacle during development of The Geysers Geothermal Field. H₂S abatement systems have evolved over the years and successful H₂S abatement to meet stringent air quality standards has become routine. The primary abatement systems for condenser vent gases are the Stretford Abatement System for surface condenser units and the burner-scrubber system for direct contact condenser units. Abatement of H₂S in circulating water is accomplished by a combination of techniques including condensate reroute, direct injection and iron chelate addition.

Achieving “ambient air quality attainment status” at The Geysers through reliable operation of H₂S abatement systems to meet operating permit limits is an underreported success story. Each of the fifteen power plants has an H₂S abatement system and a continuous tail gas process monitor. One power plant operator per unit operates the power plant and abatement system. Strategic water injection into the steam reservoir has become another important tool for reducing gas content in steam and helps reduce abatement system operating costs.

Background History of H₂S Abatement and Ambient Air Quality at The Geysers

Over the past 50 years of operations, H₂S abatement has played a critical role in the development and success of The Geysers. H₂S emissions once stalled the development of the Geysers field in the mid 1970’s and caused numerous ambient air quality exceeds for H₂S. After the development and successful implementation of H₂S abatement systems, the Geysers region has been designated as being in attainment with the California H₂S Ambient Air Quality Standard for the past 20 years. Successful H₂S abatement at The Geysers has helped geothermal earn its reputation as a clean

renewable energy resource and has become a source of pride in the geothermal industry.

In 1974, H₂S emissions were unabated on PG&E Units 1-10 that produced about 396 MW and emitted annual average emissions of about 700 Kg/hr H₂S. In contrast, today with abatement systems on all power plants and total field wide generation of more than 750 MW, the 2007-2010 H₂S annual average emissions are about 57 Kg/hr.

During the development of The Geysers field in the early 1970’s increasingly stringent H₂S emission limits were applied to achieve compliance with the California ambient air quality standard for H₂S of 0.03 ppmv (30 ppbv). The original PG&E Units 1-12 were built without consideration of H₂S abatement. To gain approval for subsequent units, power plant and steamfield developers agreed to an aggressive program of research and development of abatement systems for new plants and retrofitting existing plants with abatement systems. All new plants installed after 1975 were designed with abatement systems to meet stringent limits from day one. Some milestones in H₂S abatement at The Geysers are summarized in Table 1 included with other tables at the end of this paper.

Retrofitting Earlier Geysers Power Plants

The first Geysers power plants all had direct contact condensers and were not designed with H₂S abatement. PG&E began investigating H₂S abatement methods in 1971.^[1] Later power plant designs were heavily influenced by H₂S abatement issues especially condenser design to manage and control the split of H₂S between the vent gases and condensate phases^[2, 3].

The initial abatement systems were retrofitted to the existing plants by adding chemicals such as iron sulfate and hydrogen peroxide to the water that circulated through the condenser and cooling tower.^[4] The initial retrofitted abatement systems had a huge negative impact on power plant operations.

“With the demands to remove more and more hydrogen sulfide, the chemical system itself became a very serious problem. Use of the system significantly increased corrosion problems, clogged pipes and other cooling system

equipment, and the large volumes of sludge created led to problems such as the degradation of cooling towers and disposal of large quantities of waste. These problems, in turn, led to a severe cutback in the capacity factor.... The problems were so severe that in the mid 1970's, we essentially scrapped the designs for Units 13, 14 and 15, and went to a totally different design. We changed from the barometric direct contact condensers of earlier units to surface condensers and we adopted the Stretford process from the oil refining industry".

-- Barton Shackelford,
President of PG&E, Sept 1985. [5]

Overview of Current Power Plant H₂S Abatement Systems at The Geysers

There was an ongoing evolution of power plant and abatement system design at The Geysers. At the time of the sale of PG&E power plants to Calpine in 1999, the units were all equipped with Stretford or Burner-Scrubber systems. Over the ensuing 10 years, Calpine has continued to make incremental improvements in these systems. Current H₂S abatement systems installed on Geysers power plants are shown on Table 2.

Table 2. Current H₂S abatement systems installed on Geysers power plants.

Category	# of Units	Condenser type	Abatement System
Retrofit power plants built prior to 1980	Units 5, 6, 7/8, 11, 12	Direct contact condensers	Burner/scrubber + DOW RT-2 iron chelate/caustic
Newer power plants built since 1980	10 Calpine units 2 NCPA units 1 Bottlerock unit	Surface condensers	Stretford + secondary as needed
Aidlin	Last plant built. Startup in 1989.	Surface condenser	Burner/scrubber + DOW RT-2 iron chelate/caustic and/or ammonia

Operating parameters of Calpine's H₂S abatement systems are summarized in Table 3. Total cumulative H₂S production in inlet steam for 2007-2010 averaged about 1,319 Kg/hr or about 10,000 tons per year. About 40% of this total H₂S is treated at power plants with the Stretford process that produces elemental sulfur byproduct. The other 60% is treated at power plants with the burner-scrubber iron-chelate caustic process that produce soluble sulfur species that are returned to the steam reservoir with injected steam condensate. Both abatement systems remove over 99% of the H₂S in the vent gas. Overall about 96% of total H₂S produced is continuously removed by power plant abatement systems at The Geysers.

If left untreated, H₂S in condensate from the condensers will be air stripped in the cooling towers and released to the atmosphere. Each power plant cooling tower has its own emission limit (in Kg/hr H₂S) according to the type of plant and when it was built. The newer plants have more stringent limits. Monthly source tests are done on each power plant cooling tower to ensure compliance. Average source test results are also shown in Table 3. Cooling tower emissions at Stretford plants average about 25% of their limits. Cooling tower emissions at burner-scrubber plants average

about 50% of their emission limits. Cooling tower emissions can vary with operating conditions so targets are chosen to be able to handle process variations and assure compliance at all times.

The existing H₂S abatement systems at The Geysers are now 20+ years old. A snapshot of recent operating cost data for existing abatement systems are summarized in Table 4. H₂S abatement costs vary with the inlet H₂S loading, the partitioning of H₂S between condensate and vent gases in the condenser or "split" (which determines whether abatement occurs in primary or secondary abatement systems) and the type of abatement system at each unit. Overall variable costs were about \$5.1 million in 2009 including abatement chemicals, sulfur handling costs, propane for burner-scrubbers and abatement system maintenance. Average costs were \$0.79 per MWh or about \$0.23 per lb H₂S in inlet steam. Additional costs for O&M manpower for abatement system is estimated to be 10-20 percent of total manpower costs. An additional \$12 million was spent over the 1999 to 2009 time frame in capital and expense projects to repair, replace or upgrade equipment on the power plant abatement systems.

Abatement System Reliability and O&M Considerations

H₂S abatement is fully integrated into Geysers operations. Geysers power plants are all hybrid power plant – chemical plants. H₂S abatement is mandatory and stringent limits must be met for each unit in order to be built and to be allowed to operate. If an H₂S abatement system shuts down or can not meet its operating limits then the power plant must be shut down.

Geysers power plants are baseloaded and have achieved an average online availability of over 97% for the past 10 years. The average time between power plant overhauls has been extended to about 7 years with occasional short outages for maintenance of abatement systems and other equipment. Abatement operations have been streamlined to the point that one operator can generally operate the abatement system and power plant during most operating hours. This speaks to the high reliability of abatement systems operations and maintenance that are mandatory for a plant to operate.

Secondary abatement of H₂S in condensate with iron-chelate and peroxide was once a major operating cost. Efforts were made to optimize this process back in the 1990's.^[6] Secondary abatement to treat H₂S in condensate for surface condenser Stretford units now rarely requires any abatement chemicals. Increased bypassing of hotwell condensate through use of desuperheat water and direct injection have decreased H₂S loading in condensate to the cooling towers by up to 25%. Hotwell condensate reroute extension, i.e. routing hotwell condensate to the farthest corner of the cooling tower from the circulating water pump suction pit, has greatly increased residence time, allowing dissolved oxygen in cooling tower water to react with H₂S in condensate.

Stretford Abatement Systems

The Stretford H₂S abatement system has been very successful at The Geysers for over 30 years. Stretford is a liquid redox process based on alkaline absorption of H₂S into solution and oxidation of sulfide to elemental sulfur in a complexed ADA-vanadium solu-

tion. The vent gas from the condenser is scrubbed with Stretford solution in a venturi scrubber and then polished in a packed tower. A sulfur froth is created in the process and elemental sulfur is filtered out of solution to create a wet sulfur cake byproduct. Some highlights of Stretfords at The Geysers are:

- 15 Stretford systems installed at The Geysers during 1979-1989 time frame.
- 13 operating Stretfords today: 10 at Calpine, 2 at NCPA and 1 at Bottlerock.
- 3 different designs implemented: Parsons, Pritchard & Peabody.
- 99.99+ % H₂S removal from vent gas received from surface condensers
- Stretford operating problems are few and manageable with minimum downtime
- Vanadium handling and Stretford solution disposal have not been a major problem.
- Solution purge or desalting of thiosulfate has rarely been needed.
- Sulfur cake byproduct sold and used as soil supplement

Stretford system statistics are given in Table 5. System capacity and typical Stretford solution chemistry is shown. Some of the Stretfords were initially undersized for the H₂S loading. As steam production and overall H₂S loading has declined most Stretfords now have excess capacity which has reduced the frequency of operating problems. There is an extensive technical literature on Stretford chemistry from annual technical conferences sponsored by the Gas Research Institute back in the 1980's and 1990's that are available online. Best practices are shared among Stretford users.^[7]

Stretford O&M Improvements

A number of improvements have been made to Stretford operations to reduce operating manpower and achieve consistent

compliance. One operator can now handle most routine daily tasks for power plant operations and Stretford processing. Improvements include the following:

- **Weekly Stretford solution chemistry monitoring.** Calpine's on-site chem. Lab provides quick turnaround for monitoring Stretford solution chemistry and daily recommendations to Operations to keep the solutions within target limits.
- **Tailgas process monitoring.** Stretford tailgas is continuously monitored for H₂S with Houston-Atlas, Delmar or Teledyne monitors. The permit limit for most plants is a one-hour average 10 ppmv H₂S. This provides a very sensitive early warning of an upset condition in Stretford solution chemistry so early corrective action can be taken.
- **Reslurry processing and molten sulfur handling eliminated at most units.** Reslurrying and molten sulfur handling were once needed to get adequately clean sulfur cake byproduct. Wash sprays were adjusted on the vacuum filter systems and all quality control limits are now met for the sulfur cake byproduct without the need to reslurry or melt sulfur.
- **Filter cake drops off the filter directly into transport bins for hauling offsite.** This has helped minimize Stretford processing manpower. The bin position under the sulfur chute is adjusted with a winch as the bin fills up to distribute the sulfur.
- **Feeding liquid chemicals from totes for Vanadium, ADA.** Vanadium, ADA and soda ash additions were previously manually batch mixed from dry powder in bags or pails. The change to liquid chemical feed has reduced manpower, resulted in more consistent solution chemistry and fewer chances for operator error. (A few units are still using dry powdered Vanadium). Most units have switched from soda ash to liquid caustic feed for reasons of improved ergonomics and reduced risks of chemical exposure.

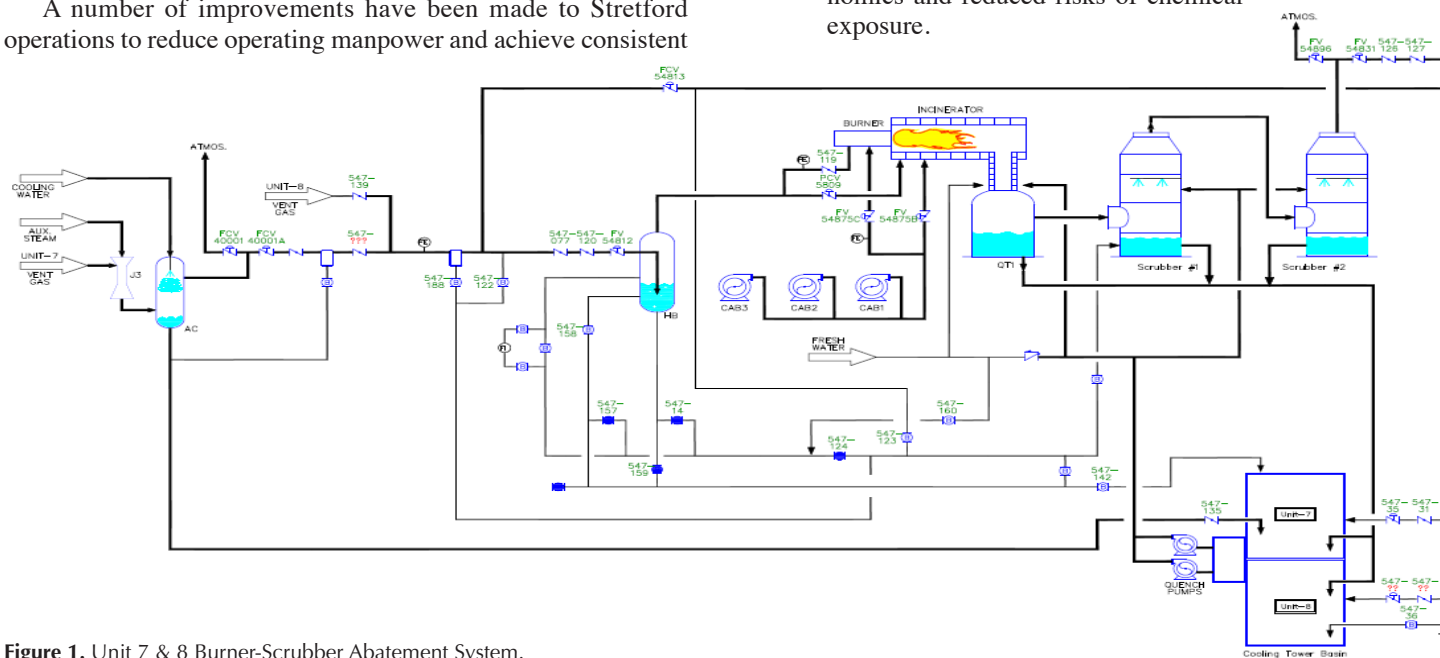


Figure 1. Unit 7 & 8 Burner-Scrubber Abatement System.

Dow Spec RT-2 on Direct Contact Condenser Units

The burner-scrubber and iron chelate abatement also known as the Dow RT-2 process, combines vent gas and condensate abatement. This process works with direct contact condenser units and is a low suspended solids process that produces soluble sulfur species that are reinjected into the steam reservoir with cooling tower blowdown. The SO₂ scrubbed out after incineration forms sulfite which then combines with elemental sulfur from the iron chelate reaction in the circulating water to form soluble thiosulfate. The burner-scrubber abatement process (combustion to SO₂ followed by water scrubbing) creates two moles of acid per mole of H₂S reacted. Some of this acid is neutralized by ammonia, a natural component of steam at The Geysers. The remainder must be neutralized by caustic additions. The burner-scrubber iron chelate system at Units 7 & 8 is shown in Figure 1.

The iron chelate dosage depends on the level of H₂S loading and the blowdown rate. Iron is lost by cooling tower blowdown and makeup is proportional to the blowdown rate. Cooling tower blowdown rates vary daily and seasonally but average about 25% on an annual average basis. Iron levels are checked once per shift and dosage adjusted to keep the target concentration of iron specified for each unit. Adjacent power plants can reduce iron chelate usage by cascading cooling tower blowdown from one unit to the next unit before final blowdown to injection. Unit 6 blowdown is cascaded to Unit 5 and Unit 7 blowdown is cascaded to Unit 8. Rerouting blowdown between adjacent units has reduced iron chelate costs at these units by about half.

In theory, two moles of iron are required per mole of H₂S contained in the condensate. In practice, the iron to H₂S ratio is reduced to less than 1.0 through extended residence time and injection of air to reoxidize and reuse the iron chelate before the condensate is stripped and H₂S emitted, in the cooling tower.

Partitioning of H₂S in Condensers

The average H₂S partitioning (split) i.e. percentage of H₂S in the vent gas for units with direct contact condensers varies from 25% to 77%. Unit 11 with the highest steam non-condensable gas (NCG) concentration of burner units has the highest partitioning averaging about 77%. Unit 12 with the lowest NCG of burner units has the lowest partitioning averaging about 25%. Units 5, 6, 7 and 8 show intermediate partitioning with rather large swings in partitioning over time due to changes in inlet NCG levels, gas composition and other process variables. Surface condensers were installed on all units that started up after 1979. Surface condensers maximize partitioning of the H₂S going to the vapor phase by avoiding the contact of the gases with the large volumes of water used in direct contact condensers. Despite the relatively high ammonia content in Geysers steam, surface condensers have provided a more consistent partitioning of H₂S into vent gas in the 70% to 86% range.

Water Injection Effects on NCG and H₂S Composition and Loading

Massive increases in injection of reclaimed water have occurred with the startup of the SEGEP* system in 1997 and with

the SRGRP** system in late 2003. Reservoir injection of reclaimed waste water has helped sustain steam production and generation since 1997. Injection at strategic locations has helped reduce both NCG and H₂S loading^[8] further reducing abatement chemical costs. For example, increasing H₂S loading at the Sonoma power plant made the Stretford system more sensitive to upset conditions such as solids loading, absorber column plugging or inlet gas fluctuations. An upgrade of the abatement system capacity was avoided by the addition of a new reclaimed water injection well. This reduced inlet H₂S levels and eliminated the Stretford capacity problem.

Bio-Assisted H₂S Abatement in Condensates

An emerging area of interest is bio-assisted H₂S abatement in condensate. So called “natural abatement” of H₂S in condensate was previously thought to be primarily due to inorganic oxidation of H₂S by oxygen in cooling tower water. However, recent observations suggest sulfur reducing bacteria naturally present in geothermal cooling tower waters can help boost abatement of H₂S and minimize the need for abatement chemical additions. This is now being investigated.

Table 1. Milestones in H₂S Emissions and Abatement at The Geysers.

1960	PG&E Unit 1 starts up in September 1960.
1960 – 1979	Units 1-12 installed with direct contact condensers. Between about 8% and up to 30% of H ₂ S in cooling tower water oxidized to elemental sulfur and soluble sulfur species by “natural abatement”. H ₂ S partitioning into vent gases was about 30-40%.
1971	PG&E begins investigating H ₂ S abatement methods.
1972	California sets ambient standard for H ₂ S at 0.030 ppmv (30 ppbv).
1975	Retrofit H ₂ S abatement methods begins with unit-scale testing at PG&E units 1, 2, 4 and 11. Abatement chemicals added to circulating water.
1975	First off-gas burner/scrubber system on PG&E Unit 4 becomes operational. Abatement level of 45% achieved.
1979	PG&E Unit 15 starts up with first surface condenser and Stretford system.
1980's	Steamfield operators retrofit steam wells with motor operated valves and install field wide supervisory control systems to minimize vented steam during plant outages.
1984	Geysers Air Monitoring Program (GAMP) implemented.
1989	Burner/scrubber units installed at Units 5/6, 7/8, 11 and 12.
1991	Attainment status achieved in Lake County for CA ambient air standard for H ₂ S.
1997	Startup of SEGEP reclaimed water injection project. Drop in NCG and H ₂ S observed.
1999	Calpine takes over operation of PG&E power plants and Unocal steamfields.
2000	Calpine installs crossover pipelines. U9/10 to U3 and U12. U3 to U19. U13 to U18 and U3 to U20. Venting of steam virtually eliminated for most of field.
2000	Unit 9 shutdown. Steam shifted to adjacent units.
2001	Unit 10 shut down. (Last iron chelate/caustic system). Steam shifted to adjacent units.
1999-2002	Direct injection and condensate reroute extensions projects installed that help to eliminate use of secondary abatement chemicals and related costs.
2002	Startup of SRGRP reclaimed water injection project. Helped suppress NCG and H ₂ S loading at multiple units.

Comparison with Other Geothermal Fields

The Geysers now has over 20 years of continuous abatement system experience on all of its power plants. Implementation of

H₂S abatement on power plants has lagged at other geothermal fields around the world. Recent technical papers speak of H₂S abatement efforts gaining momentum in other fields with implementation underway at Larderello, in Japan and Iceland.

Table 3. Geysers H2S Primary Abatement System Performance Statistics -- 2007-2010.

		Startup Date	Avg Gross MW Load	Inlet H2S ppmw	Inlet Steam H2S Loading Kg/hr	Average Split	Stretford or Burner Tail-gas ppmv	H2S in Condensate to Tower Kg/hr	Cooling Tower H2S Limit Kg/hr	Avg H2S Tower Emissions Kg/hr	
Stretford Units	Bear Canyon	Oct-88	14	125	12	84%	1.1	1.3	0.9	0.2	
	Sonoma	Dec-83	43	133	46	82%	0.7	4.8	3.6	0.3	
	WFF	Dec-88	26	125	23	84%	1.3	2.7	1.0	0.3	
	Unit 13	May-80	61	115	119	80%	1.3	10.7	6.9	2.5	
	Unit 14	Sep-80	54	67	27	82%	0.4	5.1	4.7	2.9	
	Unit 16	Oct-85	53	107	49	78%	1.9	8.8	2.3	0.6	
	Unit 17	Dec-82	54	326	144	85%	20	17.9	6.0	0.1	
	Unit 18	Feb-83	58	55	26	79%	0.9	5.5	5.2	1.5	
	Unit 19	Apr-84	67	131	74	86%	2.3	9.2	3.6	1.1	
	Unit 20	Oct-85	44	79	28	80%	0.7	5.5	4.7	0.7	
	Totals		474		547			72	39	10	98.1%
Incinerator Units	Unit 5	Dec-71	41	216	68	65%		24	11	5	
	Unit 6	Dec-71	42	269	95	68%		31	11	8	
	Unit 7	Aug-72	36	521	161	74%		42	11	7	
	Unit 8	Nov-72	38.2	132	40	54%		18	11	4	
	Unit 11	May-75	65.2	430	232	77%		53	22	11	
	Unit 12	Mar-79	53.3	106	45	25%		34	22	12	
	Aidlin	May-89	16.9	806	130	70%		39	1	0	
	Totals		292.6		772			241	89	47	94%
	Calpine Totals		766.5		1319			313	128	57	96%

Table 4. Geysers 2009 H2S Abatement Related Cost Summary.

Abatement System Type	Unit	Average H2S Inlet Steam ppmw	Annual H2S Production Lbs /Year	2009 Abatement System Cost Totals (\$000)	2009 Gross Generation mwh	2009 Abatement Related Costs \$ per mwh	2009 Abatement Costs \$ per Lb H2S Inlet
Burner	Aidlin	767.0	2,550,153	\$765	158,973	4.81	0.30
Burner	Unit 5/6	233.0	2,763,700	\$572	722,886	0.79	0.21
Burner	Unit 7/8	276.0	2,890,911	\$666	623,503	1.07	0.23
Burner	Unit 11	427.0	4,500,954	\$513	568,411	0.90	0.11
Burner	Unit 12	114.0	895,677	\$347	456,091	0.76	0.39
Stretford	Sonoma	125.0	752,837	\$245	352,995	0.69	0.33
Stretford	Calistoga	135.0	1,204,040	\$264	529,487	0.50	0.22
Stretford	Unit 13	113.0	993,626	\$239	528,175	0.45	0.24
Stretford	Unit 14	71.0	526,272	\$66	461,434	0.14	0.12
Stretford	Unit 16	107.0	832,823	\$201	449,887	0.45	0.24
Stretford	Unit 17	328.0	2,593,906	\$686	447,151	1.53	0.26
Stretford	Unit 18	51.0	456,811	\$182	487,080	0.37	0.40
Stretford	Unit 20	79.0	531,259	\$113	368,424	0.31	0.21
Stretford	Bear Cyn	130.0	237,994	\$184	125,336	1.47	0.77
Stretford	WFF	117.0	418,852	\$307	232,577	1.32	0.73
Totals		197.8	22,149,814	\$5,348	6,512,412	0.82	0.24

Wgt. Average

Average

Average

Table 5. Calpine Geysers Stretford Systems Snapshot—April 2010.

	13	14	16	17	18	20	Sonoma	BC	Calistoga	WFF
Actual sulfur loading, Long ton/day	1.1	0.6	1	3	0.5	0.6	0.9	0.3	1.4	0.5
Design Sulfur Loading, Long ton /day	6	6	6	9	6	6	2.2		3.2	
Stretford Loading, H2S Kg / Hr	36	23	29	132	20	21	40	13	63	21
Stretford Liquid Flow, gpm	2800	2800	2800	3920	2800	2600	950	500	1650	500
System Solution Volume, gallons	130,000	130,000	130,000	160,000	130,000	130,000	60,000	18,500	90,000	18,500
Thiosulfate, g/l	345	390	328	102	449	355	325	30	385	57
Anthraquinone Disulfonic Acid g/l (ADA)	1.15	0.89	1.02	0.67	0.80	0.74	0.98	1.23	1.38	1.11
Vanadium, g/l	0.95	0.81	0.92	0.61	0.82	0.70	0.74	1.11	1.02	1.02
Total Alkalinity, (Na2CO3 g/l)	34.3	33.6	33.5	27.2	34.9	31.7	32.2	33.7	35.6	34.3
Total Suspended Solids % (by Centrifuge)	0.1	0.1	0.1	1.0	0.1	0.1	0.1	2.0	0.1	0.2
pH	8.3	8.4	8.3	8.5	8.6	8.5	8.4	8.2	8.4	8.3
Boron, g/l	0.29	0.19	0.34	0.06	0.24	0.29	0.18	0.37	0.22	0.00
Green Color? 0=None, 5= Very green	0	0	0	0	0	0	0	0	0	0
Process Monitor, ppmv H2S	Tracor-Atlas	Tracor-Atlas	Tracor-Atlas	Tracor-Atlas	Tracor-Atlas	Teledyne	Tracor-Atlas	Tracor-Atlas	Delmar	Tracor-Atlas
Sulfur filter type	Belt filter	Verti-Press	Belt filter	Verti-Press	Belt filter	Belt filter	Bird Drum filter	Bird Drum filter	Plate & Frame	Bird Drum filter

Conclusion

The development of The Geysers field to date and its ongoing success depends on successful operation of its H₂S abatement systems. The implementation of H₂S abatement at The Geysers is a remarkable achievement, matched no where else in the geothermal industry in terms of the scope of abatement required and achieved.

* SEGEP = SouthEast Geysers Effluent Pipeline
 ** SRGRP = Santa Rosa Geysers Recharge Project

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