

Integrated Hybrid Cooling, Direct-Contact Condenser, and H₂S Abatement to Lower Operating Costs and Increase Injection

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ABSTRACT

U.S. Geothermal Inc. is developing a new dry-steam geothermal power plant in The Geysers which will use several novel processes and equipment designs to meet reservoir management, environmental requirements, and to minimize operating costs. The plant will use direct-contact condensers (DCC), and a burn-and-scrub system will be used for H₂S abatement. The condensing system differs from most designs with respect to its use of dry cooling and integration with the NCG treatment system. Dry cooling increases the injection of condensed steam from a typical 20% to 85% of the incoming steam. Condensate is produced in multiple zones in the DCC to control NH₃ and H₂S partitioning, and condensate is used to directly scrub most of the SO₂ from the burned gas, lowering caustic usage. This paper discusses the new design concepts and the process chemistry. Caustic costs associated with NCG treatment are anticipated to be less than 20% of a conventional burn-and-scrub system, and the value of the steam produced in the waste-heat boiler should offset most of that cost.

1. Introduction

U.S. Geothermal Inc. (USG) is developing a new geothermal power plant in The Geysers region under its wholly owned subsidiary, Western GeoPower LLC. The development location is the site of the old Geysers Unit 15 power plant. For this facility, a new, integrated design is being developed that recovers three to four times as much condensed steam as most steam geothermal power plants. This new design will be used to sustain production from the reservoir and also achieve a roughly 80% reduction in the chemical and utility operating costs associated with the treatment of the non-condensable gas (NCG), particularly for the removal of H₂S.

Figure 1 shows a schematic of the system being designed for the USG project at The Geysers. The steam is condensed in a multi-stage direct-contact condenser (DCC) system, which was designed i) to control partitioning of the NH₃ and H₂S in the vapor and liquid streams and ii) to provide a significant amount of condensate for use in SO₂ scrubbing and also for reinjection. The NCG from the vacuum system is exhausted at a pressure slightly above atmospheric. Mercury is first removed from the NCG, and then the gas is burned, converting any H₂S to SO₂. A waste-heat boiler (WHB) is used to produce additional steam for the turbine from the cooling of the hot combustion gases. A quench is used to further reduce the temperature of the gases. After the quench, the sulfuric acid mist is removed from the gas by a candle filter. The gas is then contacted in the water scrubber with a large amount of water from the steam condenser system resulting in the absorption of the majority of the SO₂ from the gas stream. Finally, the remaining SO₂ is then scrubbed out using caustic prior to the treated gas being vented into the cooling tower.

The details of the steam flow rate and non-condensable gas (NCG) composition are shown in Table 1. As is typical at The Geysers, the NCG is primarily carbon dioxide (CO₂), but also contains a substantial amount of hydrogen sulfide (H₂S), ammonia (NH₃), hydrogen (H₂), and various hydrocarbons. Minimizing emissions (e.g., H₂S, NO_x, SO_x, PM) from the facility is particularly important given the stringent environmental regulations in that area.

Table 1. Non-condensable gas characteristics

Steam flow rate, lb/hr	467,000	
NCG wt%	0.85	
NCG flow rate, lb/hr	3,969	
NCG Composition	wt%	lb/hr
Carbon Dioxide (CO ₂)	82.98	3,294
Hydrogen Sulfide (H ₂ S)	6.22	247
Ammonia (NH ₃)	1.29	51
Nitrogen (N ₂)	2.56	101
Methane (CH ₄)	6.1	242
Hydrogen (H ₂)	0.86	34

The DCC differs from typical designs. The condenser system consists of two zones, which is typical, but the water to and from the two zones is kept separate in order to manage ammonia and hydrogen sulfide partitioning. Rather than an evaporative cooling tower, a multi-cell, air-cooled water cooler (ACWC) is used to provide cold water for Zone 1 of the condenser. When cooling

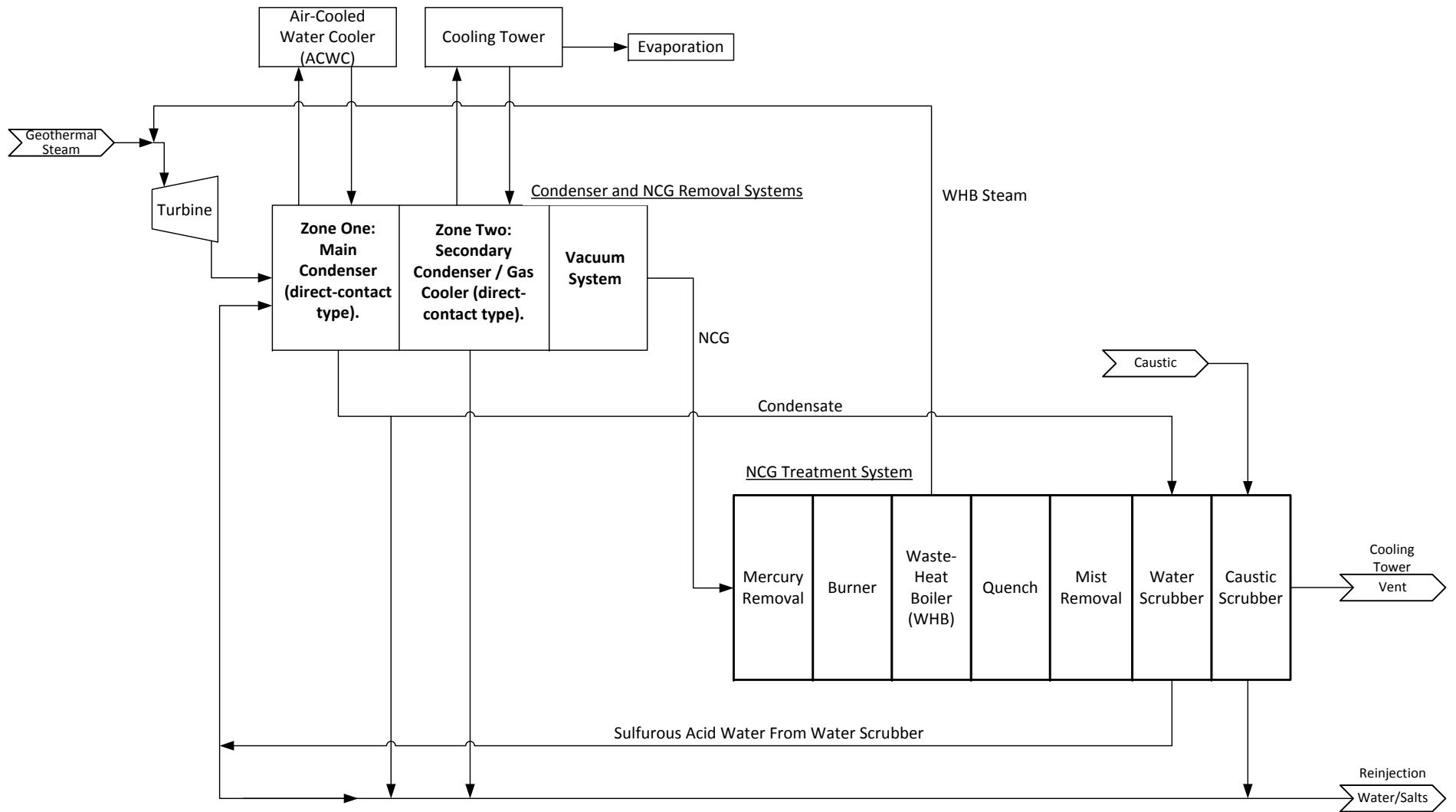


Figure 1: Simplified schematic of an integrated steam condensation and NCG treatment system

towers are used it is common for 75% to 80% of the condensate to be evaporated into the air. The use of air coolers in this design results in all of the steam condensate from Zone 1 being available for other uses. This extra water is used to absorb SO_2 from the burned NCG and is ultimately injected back into the reservoir as SO_2 , without being converted to another species, as is usual in burn-scrub systems at the Geysers. The remaining steam from the turbine exhaust is condensed in Zone 2. Recirculating water delivered to the second zone is cooled by a cooling tower. A high percentage of the water flowing to Zone 2 is evaporated, resulting in an average overall project water reinjection of about 85%.

The design of the NCG treatment system was developed holistically with the two-zone condensing system, and the two systems are configured to maximize the utility of the condensate and minimize the operating costs of the gas treatment system. Treatment of the NCG is based on the conventional “burn-and-scrub” process. In the conventional burn-and-scrub process the NCG is burned, oxidizing most of the H_2S to SO_2 , then the burned gas is quenched and scrubbed with caustic to remove the SO_2 . One important variation in the NCG treatment system developed by Trimeric and USG is the use of a WHB to provide most of the cooling duty for the hot burned gas, producing steam to generate about 250 kW of power. At a power value of eight cents per kWh, the annual value of this power would be over \$150,000/year. The new NCG treatment system also includes a small quench, a water scrubber (for bulk SO_2 removal), and a caustic scrubber (for SO_2 polishing). The high H_2S partitioning achieved in the multi-step, DCC system results in the reduction of the amount of H_2S that must be removed from the condensate going to evaporative cooling towers. (H_2S removal from condensate sent to evaporative cooling towers is referred to as “secondary abatement”.)

Compared to conventional burn-and-scrub systems this configuration has some advantages, including: more water is available for reinjection in a location where water is critical for reservoir management, and the purchase of caustic for NCG treatment is greatly reduced. The more complex condenser system and the addition of a water scrubber to the process results in an increase in the capital cost of the system, but the value of the water for reinjection, and the savings in caustic usage merit the additional capital for this case.

The remainder of this paper presents some of the conceptual elements of this process with preliminary performance results based on simulation studies. Innovations to the condensing system are presented first followed by developments for the combined use of water and caustic scrubbers for sulfur species abatement. The process presented in this paper is still in the developmental phase, the results are based on process simulations and other calculations, and changes to the design and process flow scheme may occur as the concepts are subjected to additional scrutiny.

Operating conditions in the power plant, including the condensing and NCG treatment units, will vary seasonally. Because ambient temperature and relative humidity vary, the operating temperature of air-cooled exchangers and the temperature of cooling tower water also vary. These temperatures directly affect other operations. Most (but not all) of the example data shown in the paper were generated at conditions considered typical at the location of the power plant: 60 °F at 50% relative humidity, which produces a 50°F wet bulb temperature. The data shown are not meant to reflect final design conditions, but instead reflect the general trends and effects of operating concepts.

2. Condenser System

There are different types of condenser systems that are used in geothermal power plants, including direct-contact and surface condensers. In direct-contact condensers (DCC) the steam is condensed by cooling water sprayed directly into the condenser vessel; a packing may be used to enhance the contact of the cooling water and steam. On the other hand, indirect, or “surface”, condensers are heat exchangers (e.g., shell and tube) that isolate the cooling water from the condensing steam. H_2S partitioning is defined as the fraction of the H_2S entering the condenser that stays with the vapor leaving the condenser, rather than being absorbed into the condensate. Because a large volume of recirculating condensate contacts the condensing steam, direct-contact condensers typically have lower H_2S partitioning to the gas phase (30-70% at The Geysers) than surface condensers (70-90%). Partitioning is a strong function of the presence of other species in the NCG, particularly NH_3 (Weres, 1985). NH_3 is readily absorbed in the circulating water, and can cause an increase in absorption of H_2S . For cases where NH_3 is not present, direct-contact condensers may achieve higher partitioning. For most cases, high partitioning is desired because it reduces the potential need for the treatment of the cooling water for H_2S removal (“secondary abatement”). Secondary abatement is often required to avoid the stripping of H_2S from the water in the cooling tower, resulting in air emissions.

Although DCC typically achieve lower partitioning of H_2S compared to surface condensers, their use can improve the overall thermal efficiency of the power plant because they more easily achieve a closer approach temperature between the cooling water and condensing steam. This in turn reduces the size of the cooling tower, and the circulating water flow rate. The two-zone condenser described above helps trap the ammonia in the first zone, which in conjunction with the addition of sulfurous acid to the first zone, results in less H_2S absorption in Zone 2, and therefore higher H_2S partitioning to the NCG than typical for a Geysers DCC.

Figure 2 shows a preliminary process flow diagram for the steam condenser portion for the power plant. Approximately 80% of the steam is condensed in the main condenser – referred to as Zone 1 – and the remaining 20% is condensed in a secondary condenser / gas cooler – referred to as Zone 2. Important aspects for each of these zones are discussed in more detail below.

2.1 Zone 1: Main Condenser

Zone 1 is designed to condense most (80%) of the steam. Rather than cooling the circulating water using a cooling tower, the circulating water is cooled in an air-cooled heat exchanger (referred to as the ACWC). The water from this zone is kept separate from the water of Zone 2.

In Zone 1, the steam exiting the turbine is contacted with cool water that is sprayed above a structured packing; this condenser operates in a concurrent, down-flow mode. Most of the steam condenses into the recirculating water and drains from the structured packing into a hot well. The water from the hot well is pumped through the ACWC and a mass flow equal to the condensed steam is removed for other uses, while the rest of the cooled water is recirculated back to Zone 1.

An important aspect of the process is that the condensate from Zone 1 will be used to provide water to the WHB, quench tower, water scrubber, caustic scrubber, and the sulfuric-acid-mist-removal system in the H_2S abatement process (for simplicity not all of the routings of water from Zone 1 are shown in Figure 1).

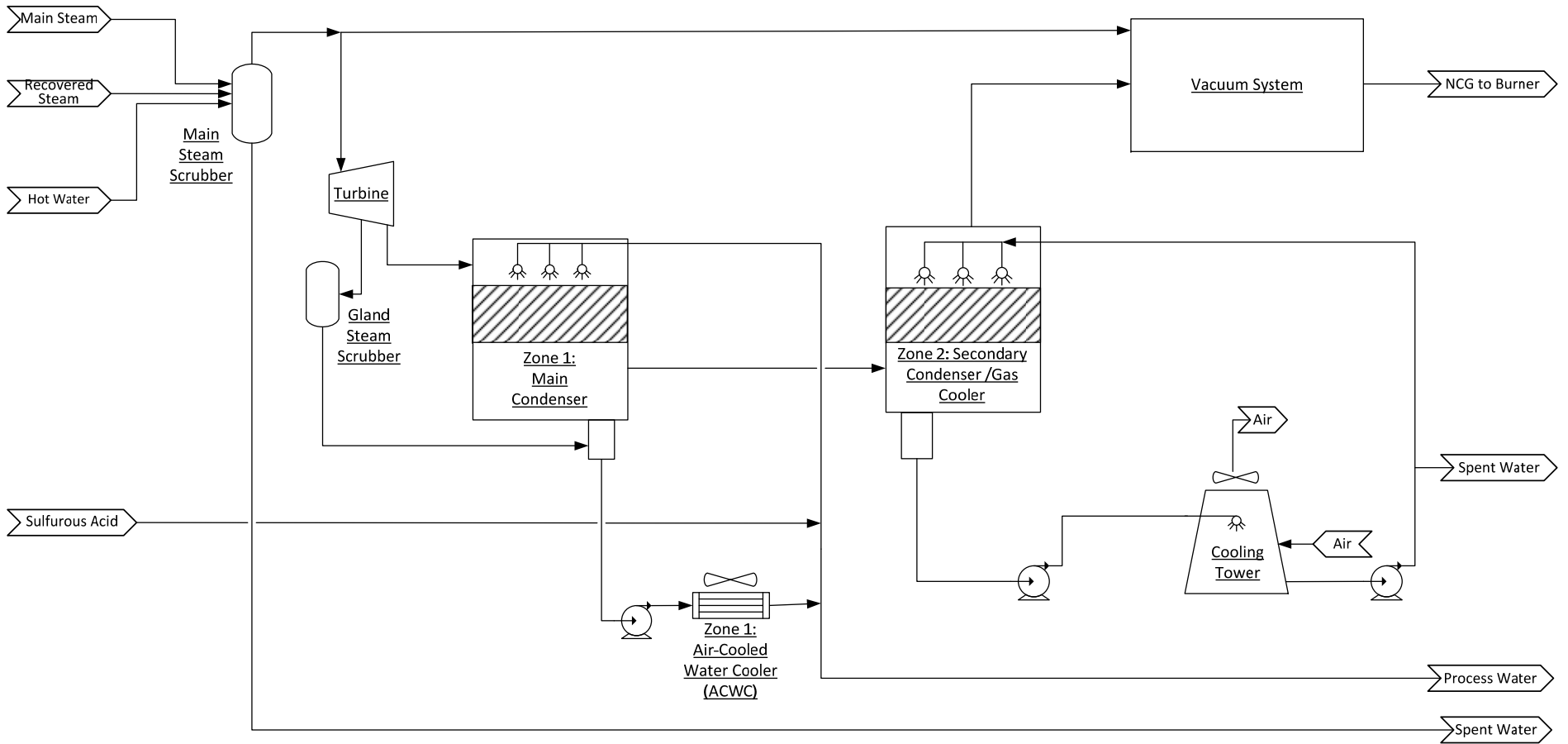


Figure 2: Preliminary process flow diagram for two-zone condenser system

The strategy to use ACWC for a large portion of the heat rejection duty represents a departure from conventional design, and presents at least two significant advantages in this application:

- A reduction of steam condensate water loss due to cooling tower evaporation, leaving more condensate available for reinjection.
- The potential for using the non-oxygenated and low H₂S steam condensate for other purposes prior to reinjection.

The main disadvantage of this design concept compared to conventional design is:

- Greater capital cost and slightly higher parasitic power load.

2.2 Zone 2: Secondary Condenser / Gas Cooler

Zone 2 is a direct-contact condenser that uses circulating water cooled by a conventional cooling tower. The purpose of Zone 2 is to condense the steam exiting Zone 1 (roughly 20% of the total steam entering the condensing system), while minimizing emissions from the cooling tower to meet the regulatory requirements for the site. This condenser has a countercurrent configuration and contains structured packing to enhance mass transfer. A countercurrent configuration is used in order to achieve the lowest possible exiting gas temperature; thereby reducing the volume of water vapor in the NCG going to the vacuum system. Additionally, the countercurrent configuration minimizes the absorption of H₂S from the steam into the water because the water exiting the contactor is exposed to the relatively low concentration of H₂S in the incoming vapor.

The drawback of the countercurrent configuration compared to concurrent is that it typically results in a greater pressure drop for the gas phase. Zone 1 is configured in the concurrent mode to take advantage of the lower pressure drop.

2.3 Effect of Acid Addition to Zone 1

The partitioning of NCG species in the condenser system has a significant effect on the performance of the NCG treatment system and on the cooling tower emissions. The NCG in the steam contains both H₂S and ammonia. Ammonia is highly soluble in water, and a large portion of the ammonia will absorb into the Zone 1 water. However, it is well-known that the presence of ammonia increases the absorption of H₂S in the water of the condenser system (Weres, 1985). As ammonia is absorbed, it raises the pH of the water which enhances the solubility of H₂S (and other acid gases such as CO₂) in the water.

It is desired to exclude H₂S from of the Zone 1 condensate since this water will be used in the NCG treatment processes. Most of the Zone 1 excess condensate will be used to scrub SO₂ from the burned NCG in the abatement system water scrubber; thus, if H₂S were present, it would be stripped out of the water and be emitted with the treated gas. To minimize the amount of H₂S absorption in Zone 1, a portion of the SO₂-loaded water (sulfurous acid) from the bottom of the water scrubber is fed back to Zone 1. SO₂ is a stronger acid than H₂S, and SO₂ will neutralize the NH₃ in Zone 1, thereby minimizing H₂S absorption. The target is to maintain Zone 1 water at a pH below about 6.5. The use of acid addition to geothermal condensers to increase H₂S partitioning has been proposed previously (Baldacci, et al., 1996), and was shown to have some benefit. This topic is covered in further detail later.

Simulations (Aspen Plus with Electrolyte-NRTL thermodynamic basis) were used to estimate the effect of sulfurous acid addition to Zone 1 condenser on H₂S and NH₃ partitioning; the (unwanted) stripping of SO₂ from the condensate into the gas leaving Zone 1 was also considered. The Zone 1 simulations were evaluated on an equilibrium basis only, assuming a single contacting stage. Mass-transfer effects (which limit the approach to equilibrium) were not included in these simulations. It is expected that mass-transfer limitations may result in the phases not reaching equilibrium in the relatively short residence time of the condenser; this equilibrium-based simulation study is meant to show the relative effects of the sulfurous acid addition to Zone 1, but not necessarily be highly accurate quantitatively. Modeling electrolyte systems can be very complicated and different simulation tools can give different results; therefore, it is critical to carefully check the simulation results against available literature data and to include the ability to tune the system to actual operating conditions.

Figure 3 shows simulation data for SO₂, H₂S, and NH₃ partitioning between the gas exiting Zone 1 and the “cooling water” (condensate plus recirculated cooled water exiting Zone 1). The graph shows the effect of the addition of varying amounts of sulfurous acid to the recirculating condensate. The addition of sulfurous acid lowers the pH of the water; the highest pH data point on the graph represents the condition at which no sulfurous acid is added to Zone 1. At neutral to acidic pH ranges, essentially all of the NH₃ is absorbed into the water, but when little or no sulfurous acid is added some of the NH₃ slips to Zone 2. Lower pH increases the absorption of NH₃ and reduces the absorption of H₂S from the vapor phase in Zone 1. Both of these affects are desired: it is preferred that little NH₃ be left in the vapor going to Zone 2 and that little H₂S is absorbed in Zone 1. However, the addition of sulfurous acid to Zone 1 has an unwanted effect: the stripping of a small portion of the SO₂ from the condensate into the vapor exiting Zone 1 to Zone 2. Depending on concentrations and pH, the SO₂ could ultimately be stripped by air in the Zone 2 cooling tower as an air emission in excess of permit limits.

It will be important to optimize the sulfurous acid feed rate to Zone 1 to maximize H₂S partitioning to the vapor exiting Zone 1, while minimizing SO₂ and NH₃ in the vapor exiting Zone 1. Figure 3 shows a region – pH in the 6 to 6.5 range – in which the desired partitioning behavior occurs to a reasonable extent.

Simulations of the combined condenser and NCG treatment systems were done to estimate the effect of the acid addition to Zone 1 on the rest of the processes, specifically emissions from the Zone 2 cooling tower and the NCG treatment system tail gas. Table 2 shows a sensitivity study evaluating the effects of acid addition rates on these key variables. As shown in the table, if the sulfurous acid (SO₂ / water solution) feed rate to Zone 1 is low (zero or 20,000 lb/hr), then there will be a significant amount of NH₃ slip with the vapor from Zone 1; this ammonia would then absorb into the water in Zone 2 and enhance the absorption of H₂S in Zone 2. If the sulfurous acid feed to Zone 1 is high (95,000 lb/hr), then there will be more SO₂ stripped from Zone 1 into the exiting vapor. In this case, most of the SO₂ in the Zone 1 outlet gas would get absorbed in Zone 2 and eventually emitted in the cooling tower (although a portion of it will likely oxidize to sulfate and be retained in the water). The use of a moderate sulfurous acid feed rate to Zone 1 (~65,000 lb/hr) results in the minimization of SO₂ and NH₃ in the Zone 1 outlet gas, and also lower absorption in Zone 2 of NH₃, SO₂, and H₂S. Low absorption of these species in Zone 2 is important since they contribute to cooling tower emissions.

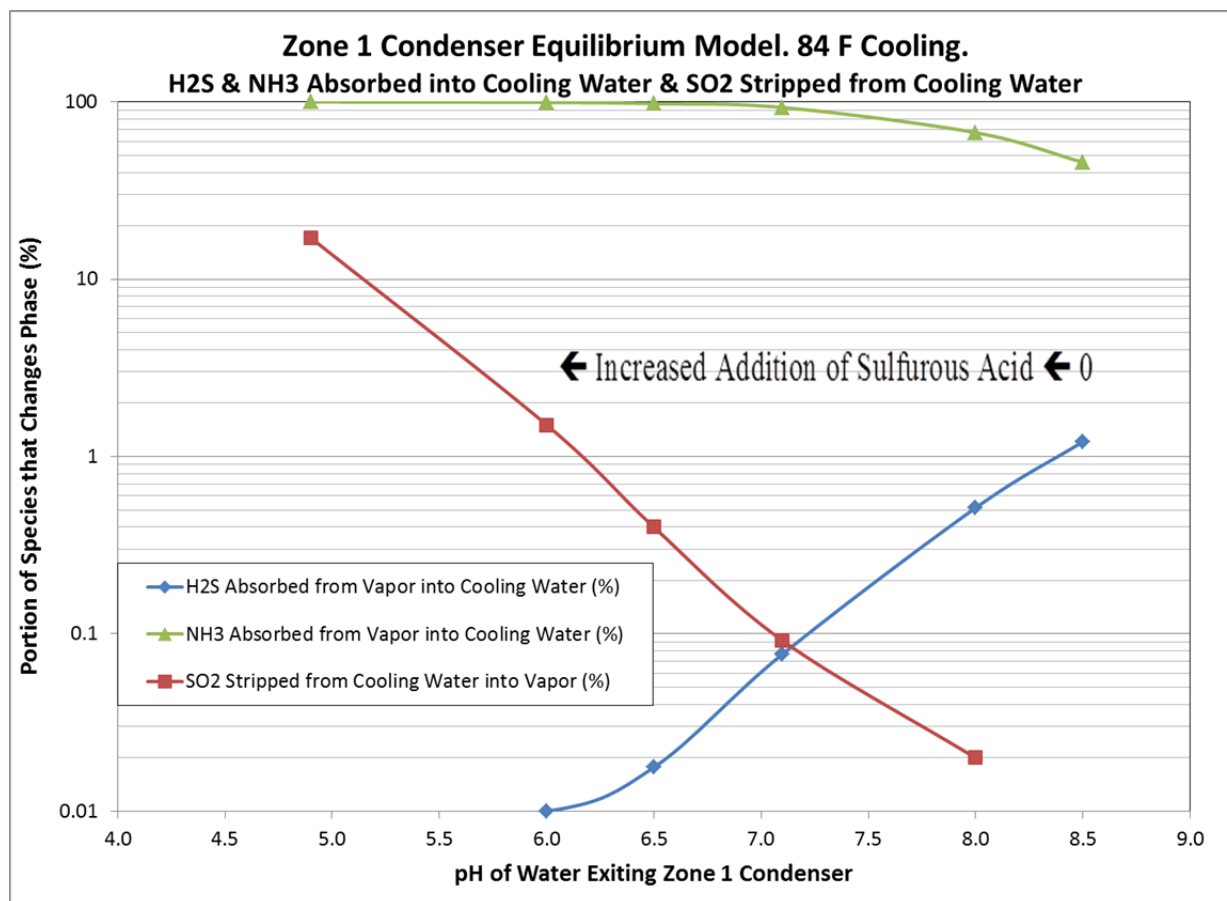


Figure 3: Species partitioning in Zone 1 (84 F, single-stage equilibrium model)

Table 2 also shows the impact of sulfurous acid addition to Zone 1 on the performance of the NCG treatment system water scrubber. As sulfurous acid is added to Zone 1 it results in the feed water to the water scrubber being pre-loaded with SO₂, which reduces its performance for SO₂ removal from the burned NCG. SO₂ that is not removed in the water scrubber is then removed from the gas in the caustic scrubber. It is desired to scrub as much SO₂ as possible in the water scrubber to minimize caustic consumption. If no sulfurous acid is added to Zone 1, then a substantial amount of H₂S is absorbed in Zone 1, and (because SO₂ has a higher water solubility than H₂S and is a stronger acid) much of this H₂S is stripped out of the water in water scrubber. Due to the presence of CO₂ in the NCG treatment system tail gas, the caustic scrubber cannot operate at conditions that would allow for the absorption of H₂S, so most of the H₂S desorbed from the water in the water scrubber is emitted to the atmosphere with the NCG system tail gas.

2.4 Optimization of Zone 2 to Minimize Cooling Tower H₂S Emissions

The amount of H₂S absorbed into the condensate should be small compared to most conventional direct-contact condenser systems. However, because of stringent environmental permits, the absorption of even a few pounds per hour of H₂S in Zone 2 can result in the need to implement secondary abatement technology in order to avoid H₂S emissions from the cooling tower higher than the permit level, which is less than 2.5 lbs/hr. It is desired to avoid, or at least minimize the cost of, secondary abatement.

Table 2. Estimated distribution of gas components in Zone 1 and Zone 2, and performance of water scrubber (base case Zone 2 cooling tower flow rate of 3.4 MMlb/hr)

Zone 1	Sulfurous acid addition to Zone 1 (lb/h, 0.25% sol'n)	0	20,000	50,000	65,000	75,000	95,000
	Cooling Water Exiting pH	8.5	8.0	7.1	6.5	6.0	4.9
	Molar Ratio, SO ₂ added : NH ₃ in feed steam	0	0.26	0.65	0.84	0.95	1.2
	Steam condensed in Zone 1 (%)	80	80	80	80	80	80
	NH ₃ absorbed into cooling water (%)	46	67	93.0	97.8	99.3	>99.9
	H ₂ S absorbed into cooling water (%)	1.2	0.5	0.08	0.02	<0.1	<0.1
	SO ₂ stripped from cooling water to vapor (%)	n/a	<0.1	0.1	0.4	1.5	17
	SO ₂ stripped from cooling water to vapor (lb/h)	n/a	<0.1	<0.1	0.7	2.8	40
Zone 2 / CT Emissions (without secondary abatement)	CTW pH (exiting cooling tower)	9.5	9.4	7.2	4.3	4.2	3.9
	NH ₃ absorbed into cooling water (%)	54	33	7.0	2.2	0.7	<0.01
	NH ₃ emissions from CT (lb/h)	22	13.2	0.1	0	0	0
	H ₂ S absorbed into cooling water (%)	15.6	14.4	12.6	12.4	12.4	12.4
	H ₂ S absorbed into cooling water & emitted from CT (lb/h)	37.7	35.3	31.0	30.6	30.6	30.6
	SO ₂ emissions from CT (lb/h)	0	0	0	0.1	1.8	33
Water Scrubber Performance	H ₂ S in gas leaving scrubber (lb/h)	1.7	0.7	0.2	0.1	0.06	0.05
	SO ₂ scrubbed by water scrubber (%)	94.4	93.9	92.1	90.3	89.0	88.5
	SO ₂ in gas leaving scrubber to NaOH scrubber (lb/h)	2.5	4.8	12.8	20.9	26.7	29.3

Process simulations were used to study the effect on H₂S absorption of variations in operating parameters and the mechanical configuration of Zone 2. H₂S absorption into the Zone 2 water can be minimized a number of ways:

- *Addition of sulfurous acid to Zone 1:* As discussed in the previous section, the addition of sulfurous acid solution to Zone 1 results in nearly all of the ammonia being absorbed in Zone 1 rather than in Zone 2; eliminating the NH₃ from the vapor entering Zone 2 reduces the driving force for H₂S absorption in Zone 2.

- *Separation of the condenser into two zones:* The absorption of H₂S in the condensers is driven by many factors including the concentration of H₂S in the vapor phase, and the amount of water present relative to the amount of H₂S. By dividing the condenser into two zones, H₂S absorption can be minimized due to the following factors:
 - In Zone 1 a very large volume of water is recirculated to condense the bulk of the steam. However, because ~20% of the steam is left uncondensed the concentration of H₂S in the exiting vapor is not very high (0.15 vol%), so the resulting equilibrium solubility of H₂S in the water (and driving force for mass transfer) is also not very high.
 - In Zone 2 a smaller volume of water is recirculated to condense the remaining ~20% of the steam. The H₂S concentration in the gas exiting Zone 2 is higher (3 to 4 vol%), but because this higher concentration of H₂S is contacted with the relatively small volume of water used in Zone 2, the amount of H₂S absorbed into the condensate is small relative to the amount that would be absorbed in a single condenser.
 - Zone 2, where the driving force for H₂S absorption is highest, is configured as countercurrent while Zone 1 is concurrent. In Zone 1 the lower pressure drop of concurrent flow can be taken advantage of since the H₂S concentration in the vapor is low. On the other hand, countercurrent contacting is important in Zone 2 in order to avoid having the water exiting Zone 2 contact the high H₂S concentration vapor.
- *Control of condensation:* In Zone 2 the amount of H₂S absorbed into the condensate is a strong function of the amount of water vapor allowed to leave with the NCG. In order to avoid excessive parasitic load in the vacuum system it is desired to minimize the amount of water vapor in the NCG entering the vacuum system. However, the condensation of nearly all of the steam results in high H₂S absorption. It is necessary to balance both the vacuum system parasitic load and the H₂S absorption in Zone 2. Evaluations to-date suggest that the cost of additional ejector steam has a lower cost than secondary abatement, and is less subject to chemical balance upsets.
- *Control of water recirculation rate and temperature:* The amount and temperature of the water recirculated to condense the Zone 2 steam is an important factor in determining the amount of H₂S absorbed into the water. The amount of water recirculated should be limited to only the amount required in order to achieve the desired condensation efficiency. The amount of water recirculated and its temperature, and the extent of vapor condensed are directly related. Control strategies will be implemented to control the water flow to achieve the desired water vapor concentration in the NCG exiting Zone 2.
- *Addition of a strong acid:* The addition to Zone 2 of an acid stronger than H₂S can marginally reduce the absorption of H₂S in Zone 2, by limiting the H₂S solubility to its molecular species. However, the addition of sulfurous acid to Zone 2 cannot be done to

the propensity of SO₂ to be stripped in the cooling tower. Sulfuric acid (low vapor pressure) could possibly be used; since some sulfuric acid will likely be recovered from the mist removal unit operation it may not result in an increase in chemical cost.

A simulation study was used to evaluate the impact of some Zone 2 design and operating conditions on the emissions of H₂S from the cooling tower (assuming no secondary abatement technology is implemented). Some data from the Zone 2 study are shown in Table 3.

Table 3. Zone 2 Simulation Study of H₂S Absorption.

Water Recirc Rate	Water Recirc Temp	H₂SO₄ Addition?	pH of Water to Zone 2	Water Vapor in Exiting NCG	Temp of Vapor Exiting	H₂S in Water to Cooling Tower
(MM lb/h)	(F)	(Yes/No)		(mol %)	(F)	(lb/h)
3.1	67	Yes	5.4	34	66	26.2
2.75	67	Yes	5.3	34	66	21.8
2.6	65	No	6.6	32	65	16.2
2.6	65	Yes	5.3	32	65	11.1
2.5	65	Yes	5.3	47	78	1.1
2.5	66	Yes	5.3	67	90	1
2.5	67	Yes	5.3	76	94	0.9
2.4	64	Yes	5.2	58	85	1
2.4	64	No	6.5	59	85	1.3
2.4	65	Yes	5.3	71	92	0.9
2.4	66	Yes	5.3	78	95	0.9

A number of other parameters not covered in Table 3 were also considered, including the depth of packing used in Zone 2, and splitting of Zone 2 into two packed sections (larger cross sectional area on the bottom and smaller cross sectional area on top). One parameter shown to be beneficial in the minimization of cooling tower H₂S emissions is to air strip the water from the Zone 2 scrubber prior to the cooling tower. Simulation studies were formulated in which the air to be fed to the H₂S incinerator was first used to strip the Zone 2 water in a packed tower. Typically about 1/3 to 2/3 of the H₂S in the Zone 2 water was removed into the stripping air; the H₂S in the stripping air would be destroyed in the incinerator, thus removing it as a potential emission source.

Overall, this study concluded that the most effective way to minimize H₂S absorption into the Zone 2 water was to limit/control the condensation of steam. Controlling the condensation is achieved by controlling the flow rate and/or temperature of the water recirculating to Zone 2 from the cooling tower. Most significantly, providing a much-higher-than-necessary flowrate of water to Zone 2 results a drastic increase in H₂S absorption. For this system at the basis conditions, careful control of condensation in Zone 2 such that the vapor exiting consists of at least 50% water vapor can result in the H₂S absorption in Zone 2 being less than a few pounds per hour. Air stripping can be used to reduce the H₂S in the water further prior to the cooling

tower. This optimization study found that the H₂S absorption in Zone 2 could be greatly reduced from the baseline data (shown in Table 2), perhaps low enough to avoid the need secondary abatement.

Intentionally limiting the steam condensation in Zone 2 will result in the parasitic energy load and equipment size in the vacuum system being larger than it would be if Zone 2 was operated to condense as much steam as possible. This negative result of limiting steam condensation is likely made acceptable by the large reduction in H₂S absorption in Zone 2. It is possible that using the above strategy can result in elimination of the need for secondary abatement, or at least a large reduction in the cost of secondary abatement. However, it should be noted that these results were obtained in simulation studies and have not been validated in laboratory or pilot plant studies.

2.5 Secondary Abatement

If the H₂S emissions from the cooling tower are higher than the permit limits, then secondary abatement could be used to lower the emissions even further. A conventional technology (“RT-2”) used for secondary abatement involves the addition of chelated iron and caustic scrubber blowdown to the recirculating cooling water. This technology, along with some alternate technologies, is being considered if secondary abatement is required. Descriptions of the iron chelate technology can be found in the literature (Bedell, 2004). One potential issue with the application of conventional secondary abatement is that the amount of SO₂ that will usually be scrubbed in the caustic scrubber is relatively small (because most of it can be scrubbed by water prior to the caustic scrubber), and under some conditions there may not be enough sodium sulfite present in the caustic scrubber blowdown to satisfy the secondary abatement stoichiometric requirements. Modification of the water scrubber and caustic scrubber designs may be required to integrate it fully with the secondary abatement system.

3. NCG Treatment System

Figure 4 shows a simplified process flow scheme for the NCG treatment system. Important features of the systems are discussed in the subsections below. The features of the system that differ from conventional technology are described in more detail, whereas those features that rely on standard configuration are covered in less detail.

3.1 Hg Removal, Incinerator, Heat Recovery, and Sulfuric-Acid-Mist Control

The gas exiting the condenser gas removal system may first be treated (if determined to be necessary) for mercury removal using a standard sulfur-impregnated carbon bed or other technique. After a flame arresting device, the gas flows to an incinerator where it is combusted using air. All of the combustible components (mainly H₂S, H₂, and methane) are oxidized. The incinerator is designed and operated to achieve near-total H₂S oxidation with the majority converting to sulfur dioxide (SO₂), although some sulfur trioxide (SO₃) will also be produced. The combustion gases will be cooled in a waste heat boiler (WHB) to produce steam that can be added to the steam supply to the turbines. The advantages of waste-heat recovery in the burn-and-scrub process are discussed elsewhere (Avery, 2015). Corrosive sulfuric acid (H₂SO₄) mist can form from SO₃ as the burned gases are cooled; the temperature of the gas exiting the WHB is

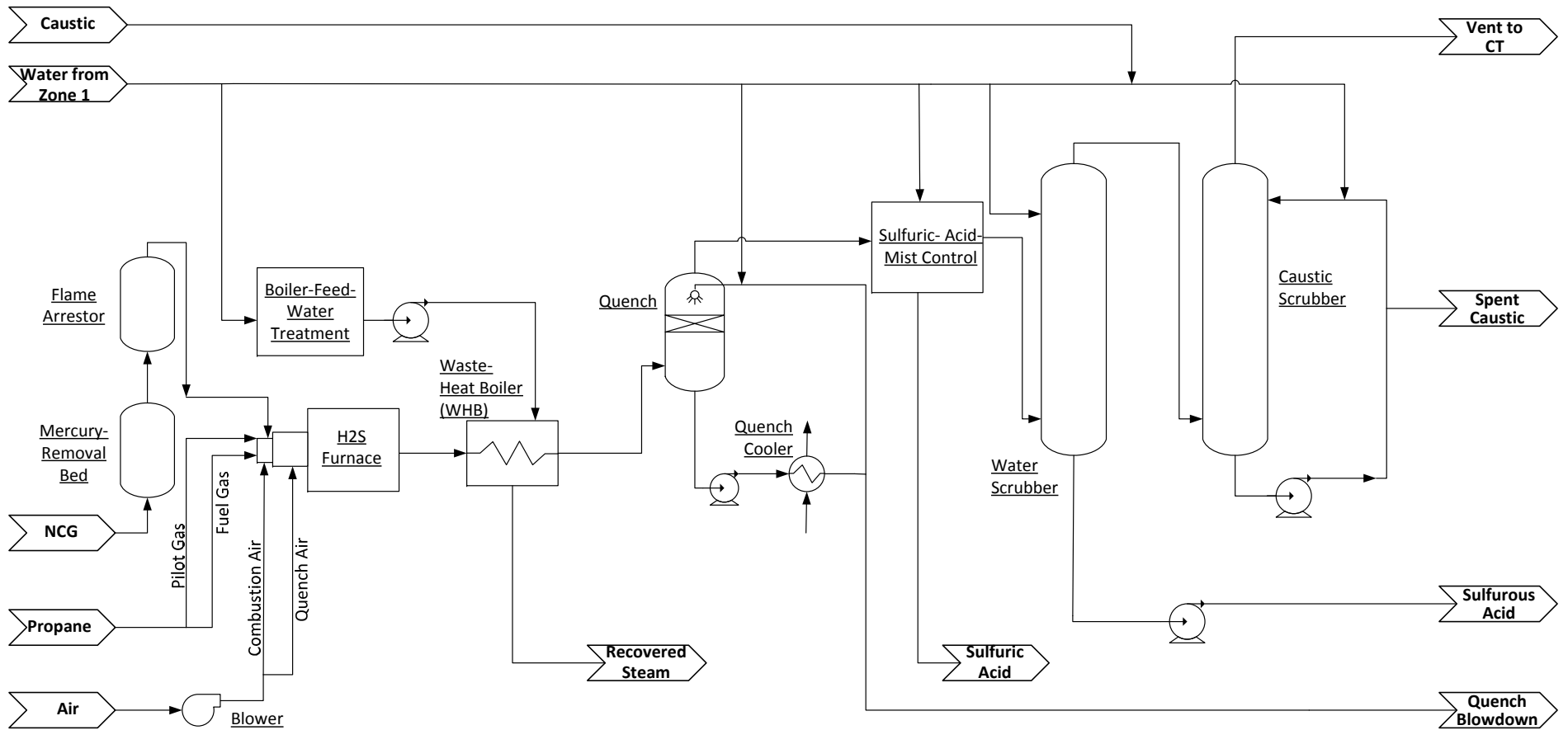


Figure 4: Simplified process flow diagram for the NCG treatment system

controlled such that it is maintained at about 50-100 °F above the acid dewpoint temperature (often in the 350 - 400 °F region).

From the WHB, the gas will pass through a quench to further lower the temperature of the combusted gas. It is anticipated that the quench combined with the downstream water and caustic scrubber will probably reduce the concentration of sulfuric acid mist in the gas substantially; however it is difficult to predict the removal efficiency of sulfuric acid mist in such devices. In order to ensure attainment of particulate emission (PM) limits, a sulfuric-acid-mist removal system will likely be installed between the quench and water scrubber. The removal of the acid mist prior to the water scrubber also helps maximize the amount of SO₂ that can be absorbed into the water because sulfuric acid absorbed into this water would proportionately exclude SO₂. Fiber-bed candle filters and wet electrostatic precipitators (WESP) are technologies commonly employed to remove sulfuric acid mist from gases. Gas from the acid-mist-removal device then flows to the water scrubber.

3.2 Water Scrubber

The water scrubber is a key feature of the NCG treatment process, and is an unusual feature compared to conventional burn and scrub system design. SO₂ has a low solubility in water, particularly given the low pressure (slightly above atmospheric) and low gas-phase concentration at which the scrubbing is carried out. Therefore, water is usually not considered an effective media for SO₂ scrubbing. However, water can be used effectively for SO₂ scrubbing if i) a very large amount of water is available at low cost, and ii) the SO₂-laden water exiting the scrubber can readily be disposed of without treatment. The hybrid condenser system, and need to inject water at the project satisfy both of these prerequisites.

The Zone 1 condenser system will produce about 300,000 lb/hr of water that can be used in the NCG-treatment systems and other areas of the power plant; eventually all of this water would be reinjected. In this study it was estimated that at least 200,000 lb/hr of water would be available for use in the water scrubber to absorb SO₂; relative to the flow rate of SO₂ in the burned NCG (about 464 lb/h), this amount of water is sufficient to absorb the majority of the SO₂ from the NCG. Note that as the water temperature from the ACWC varies across the year, the amount of absorbed SO₂ varies, and therefore affects the amount of caustic required.

The temperature of the water feeding the water scrubber will be the temperature of the Zone 1 cooling water exiting the ACWC; the temperature to which Zone 1 can be cooled will vary seasonally, and it is expected to produce water with a range of about 73 to 130 °F; the design basis (typical) temperature for this water is 84 °F. Typically, the temperature will be run as cool as can be practically achieved with the ACWC, with a lower limit of roughly 70 °F. Lower temperatures are preferred since it benefits the efficiency of the power plant as well as the efficiency of the water scrubber for SO₂ removal.

3.2.1 The Solubility of SO₂ in Water

Because the use of the water to absorb SO₂ is a key aspect of the process, particular care was taken to ensure that the solubility of SO₂ in water was well-represented in calculations. Initial work showed large disagreements in water scrubber performance using various methods, so we investigated this issue in depth.

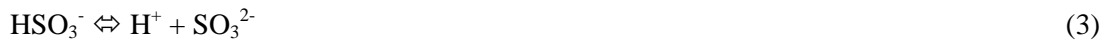
At low to moderate pressures, the solubility of SO₂ in water is usually described by Henry's law. The equation for Henry's law can be written in many ways, but basically it states that the solubility of a gas is proportional to its partial pressure in the gas phase. For example:

$$H = x_i/p_i \quad (1)$$

Where H is the Henry's law constant, x_i is the liquid-phase mole fraction of SO₂ and p_i is the gas phase partial pressure of SO₂. Henry's constants, including terms for temperature variation (which is very important), are found in the literature (Sander, 2015). Experimental data for the solubility of SO₂ in water can also be found (Seidell, 1919).

Although the use of Henry's law is a valid approach to describe the solubility of SO₂ in water under most conditions, it was found that care must be taken when using Henry's law at the very low SO₂ partial pressures typical of the water scrubber. Henry's law models the solubility of the molecular form of the solute, but does not take into consideration the effect of dissociation / hydration of gas species in aqueous solution. For gases like oxygen and methane this is not an issue. However, for gases that participate in electrolyte equilibrium in water, this can result in Henry's law not modeling the solubility of the solute well, unless the dissociation is taken into consideration.

SO₂ hydrates and dissociates to some extent in water, as described by the reversible equilibrium chemistry below:



When SO₂ is dissolved in pure water, at low to moderate partial pressures, the extent of reaction 3 is usually small. However, the product of reaction 2 (HSO₃⁻) can represent a significant portion of the total SO₂ that is dissolved in the water at low partial pressures of SO₂. The dissociation of SO₂ in solution can be described by an equilibrium constant, K_a . Because SO₂ in aqueous solution can undergo two dissociations, there are two K_a values that describe it (K_{a1} and K_{a2}):

$$K_{a1} = \frac{[\text{H}^+][\text{HSO}_3^-]}{[\text{SO}_2]} \quad (4)$$

$$K_{a2} = \frac{[\text{H}^+][\text{SO}_3^{2-}]}{[\text{HSO}_3^-]} \quad (5)$$

K_a values are often represented in the literature as $\text{p}K_a$, which is defined as:

$$\text{p}K_a = -\log_{10}(K_a) \quad (6)$$

The first $\text{p}K_a$ – which is also the pH at the extent of completion of reaction 2 is 50% – of SO₂ in water at 25 °C is 1.89 (Dean, 1972).

If the dissociation is not taken into consideration, and Henry's law is used to represent the total solubility of SO₂ in water, the SO₂ solubility can be under-predicted. To better predict the solubility of SO₂ in water, the extent of reactions 2 and 3 would need to be calculated

concurrently with equation 1 so that only the molecular species of SO_2 in aqueous solution is used in equation 1. *Note that this factor is only important at rather low SO_2 partial pressures where the concentration of dissociated species is significant relative to the dissolved molecular species.*

To illustrate the importance of this issue, Figure 5 shows the Henry's law constant for SO_2 calculated from experimental data (Seidell, 1919) across a range of SO_2 partial pressures up to about one atmosphere. The blue line shows Henry's law constant values calculated for each experimental data point directly. As the partial pressure of SO_2 becomes less than about 2 psi, the Henry's constant is clearly no longer constant. However, if the dissociation equations are used with published pK_a values to calculate the extent of dissociation, and the molecular SO_2 concentration is only used to calculate the Henry's constant, then the Henry's constant at low partial pressure becomes a much more constant value (green line). For comparison, a literature Henry's constant (Sander, 2015) is also shown on the graph (black line).

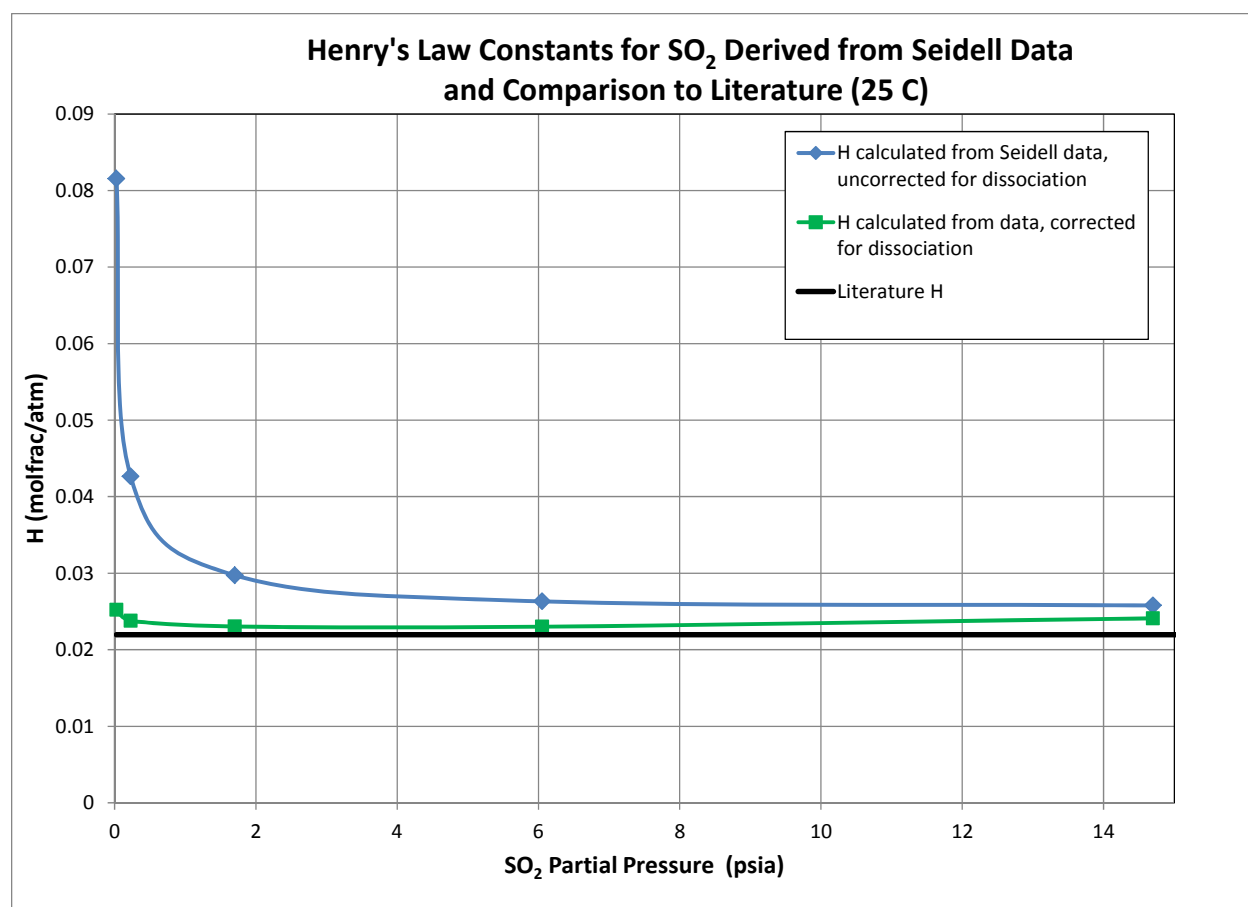


Figure 5. Henry's Law Constants Calculated from Data at Varying SO_2 Partial Pressures.

The partial pressure of SO_2 in the burned NCG entering the bottom of the water scrubber is expected to be roughly 0.5 psia. Thus, because of the effect seen in Figure 5, we located SO_2 solubility data at low partial pressure in the literature to check the process simulation output. For the SO_2 -water system, Aspen Plus process simulations using electrolyte-NRTL properties gave

reasonable results compared to the literature in the prediction of SO₂ solubility at low partial pressures, so this software was routinely used to predict this system.

The above discussion was based on a system of pure water and SO₂. The actual water scrubber will contain other components in the gas and liquid phases. Ammonia, SO₂, H₂S, CO₂, and other components will be present in the scrubber in both phases, and the presence of these other species can affect the scrubbing efficiency of SO₂ from the burned NCG.

3.2.2 Design Parameters

Because the water scrubber relies on the solubility of SO₂ in water, rather than acid-base reactions of a caustic scrubber, the efficiency of water scrubbers tend to be low, in that it is more difficult for the scrubbers to obtain equilibrium between the gas and liquid phases. In order to ensure a reasonable SO₂ removal efficiency, the water scrubber was designed with a relatively high packed bed height compared to shorter packed beds that are typical of chemical-reaction-driven scrubbers like caustic scrubbers.

The overall mass transfer coefficient (K_{ga}) for SO₂ absorption into water is about one-fourth that for SO₂ absorption (enhanced by chemical reaction) into a base (Strigle, 1994). This implies that roughly (all other variables being equal) four times as much packed height is required for a SO₂ water scrubber to achieve the same approach to equilibrium as for a SO₂ caustic scrubber.

The water scrubber is once-through with respect to both the gas and water phases. Most scrubbers that rely on acid-base reactions maintain a large recirculation loop of liquid, often to help enhance mass transfer and/or control heat of reaction affects. Liquid recirculation can be used in a caustic scrubber because the caustic strength is usually maintained such that the equilibrium vapor pressure of SO₂ is extremely low, and the difference between the liquid at the top and bottom of the column is small. However, because the water scrubber for SO₂ removal relies on physical solubility, only fresh water should be fed to the top of the column in order to avoid having a high SO₂ vapor pressure in the liquid at the top of the column.

3.3 Caustic Scrubber

The bulk of the SO₂ in the combusted gas stream is removed by the water scrubber, even in the summer when the water being fed to the water scrubber is warmest. As shown in Figure 4, the caustic scrubber has a liquid recirculation loop, with makeup caustic being added and blowdown removed from the recirculation loop. Caustic is added continuously to maintain a moderate pH in the recirculating caustic: in the roughly 6 – 8 range. Maintenance of this moderate pH results in both i) scrubbing of the SO₂ down to low levels and ii) minimizing the scrubbing of the CO₂ contained in the gas stream. If the pH were maintained at a higher level, more of the CO₂ would be scrubbed resulting in greatly higher caustic usage. The SO₂ dissolved in aqueous solution reacts readily with the sodium hydroxide to form a solution of sodium bisulfite (NaHSO₃) and sodium sulfite (Na₂SO₃), the ratio of which depends on the amount NaOH added relative to the amount of SO₂ scrubbed. Both of these salts have significant solubility in water.



One of the complications of this proposed highly-integrated system design is that a small amount of H₂S will be contained in the water that is condensed in Zone 1. As a first-order approximation, all of this H₂S will be stripped out of the water in the water scrubber, and this H₂S in the gas phase will then go to the caustic scrubber. Caustic scrubbers can easily be designed to scrub H₂S from gases. However, for this case it is not practical to design the caustic scrubber to remove most of the H₂S. CO₂ and H₂S have similar acid-base properties and under equilibrium conditions CO₂ will absorb into caustic with roughly the same efficiency as H₂S. Maintenance of the caustic scrubber solution at a moderate pH is done to minimize the absorption of CO₂ from the gas, but it also results in much of the H₂S not being absorbed into the caustic scrubber and thus being emitted to the atmosphere with the treated gas.

Because of the difficulty in dealing with H₂S in the gas in the NCG treatment train after the burner, it is important to design and operate the Zone 1 condenser to minimize the absorption of H₂S into the water, because a significant portion of H₂S that is absorbed in Zone 1 will eventually be emitted with the treated burned NCG.

The use of a water and caustic scrubber arrangement greatly reduces the caustic chemical costs compared to a traditional burn-and-scrub process. With a traditional burn-and-scrub system all of the SO₂ would be treated in the caustic scrubber with an approximated annual chemical cost of about \$1 MM/yr. However, with this novel arrangement the bulk of the SO₂ is removed in the water scrubber such that the caustic costs should be less than approximately 20% of that expected with a traditional burn-and-scrub unit. Additional chemical costs may also be required for secondary abatement (e.g., for iron chelate) if necessary, but they should be a relatively small fraction of that used in conjunction with a conventional burn-and-scrub process.

4. Conclusions

The novel condensing and H₂S abatement concept presented here offers several potentially significant improvements over the more typical condensing and burn-and-scrub processes traditionally used at power plants as indicated below.

Increased Steam Condensate for Injection

Because air-cooled exchangers are used to cool part of the water used in the direct-contact condensers, more condensate is available for use than what would be available with commonly used cooling tower designs (due to losses through evaporation). The overall injection rate from the plant is about 85%, compared to 15% to 25% for a typical geothermal steam power plant using steam condensate in evaporative cooling towers.

Control of Water Chemistry and Gas Absorption/Partitioning

Another important aspect of design is that the excess cooling water (blowdown) from Zone 1 is very low in H₂S (approximately 1 ppm) because adding sulfurous acid to Zone 1 causes essentially all of the NH₃ to be absorbed into the circulating water while leaving nearly all of the H₂S in the non-condensable gas that flows to Zone 2 of the condensing system. Additionally, limiting the condensation in Zone 1 also reduces the partial pressure of H₂S in the vapor leaving the zone, thereby reducing the driving force for mass transfer of H₂S from the vapor to the

condensate. The operation of Zone 1 to minimize H₂S absorption allows for the practical use of the excess cooling water (condensed steam) to scrub SO₂ from the burned NCG.

Minimal Secondary Abatement Requirement

There are many operational and equipment design features that can be implemented in Zone 2 to minimize emissions from the cooling tower. Even with these changes, if the emissions from the cooling tower are still higher than the permit limits, then secondary abatement could be used at a much lower cost for chemicals than that of a conventional system (because of the smaller amount of water and dissolved H₂S that has to be treated compared to a conventional system).

Lower Caustic Costs

In this design the majority of the SO₂ is removed with water and the caustic scrubber is only required to remove a fraction of the SO₂. The caustic costs for the combined water/caustic scrubber system are expected to be less than 20% of the cost anticipated for a traditional burn-and-caustic-scrub system.

There are still some details of the new integrated steam condensing and burn-and-scrub process that have not been finalized. However, these improvements suggest operating cost savings that could readily offset any capital expenses for special equipment design. This could make the new process an attractive alternative to the more traditional burn-and-scrub approach.

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