Bulletin d'Hydrogéologie No 17 (1999)
Centre d'Hydrogéologie, Université de Neuchâtel
EDITIONS PETER LANG

Controlling H_2S emissions in geothermal power plants

by Gary J. Nagl

USFilter/ Gas Technology Products, 1501 East Woodfield Road, suite 200W, Schaumburg, IL 60173, USA

ABSTRACT

Geothermal power plants are environmentally attractive since they employ a renewable energy source; however, geothermal steam contains varying amounts of noncondensable gases (NCG), such as carbon dioxide (CO,) and hydrogen sulfide (H_2S) which, if not dispose of correctly, may cause environmental, health and safety problems. Also, if the carbon dioxide **is** to be further processed to produce beverage grade carbon dioxide, the hydrogen sulfide must be removed to extremely low levels. In some locations, H_2S is present in sufficient quantities to represent a reasonable raw material for producing elemental sulfur, which can be sold as a product for producing sulfuric acid or fertilizers.

This article describes various methods for controlling hydrogen sulfide emissions in geothermal power plants. The technical aspects of each system are described in detail, in addition, to disposal of the byproducts produced by each system, which has become a major consideration in Europe.

KEYWORDS

Hydrogen sulfide, noncondensable gas, LO-CAT, Sulfur-Rite, scavenger

1. Noncondensable gas generation

Geothermal systems are classified either by enthalpy (heat content) or by the physical phase of the geothermal fluid. High enthalpy or vapor dominated systems, such as the Geysers in northern California, are well suited for the production of electrical power while the more common low enthalpy or water dominated systems are well suited for direct heat uses. Depending on the classification of the geothermal system, electric power is generated in either conventional steam turbine plants or in binary plants. Steam turbines are generally used for systems with fluid temperatures greater than 150°C, and binary units are used for systems **less** than 150°C.

Conventional steam turbine units can be of the back pressure or condensing type. In the back pressure type, the turbine exhaust **is** simply vented to the atmosphere, which results in an inexpensive but very inefficient operation. The more common condensing turbine, shown schematically in Figures 1 and *2*, **is** more expensive than a back pressure turbine; however, it is approximately twice as efficient. In this type of unit, the mixture of steam and brine (salt water) from the production wells is flashed and separated. The separated brine is reinjected which provides a continual source of fluid for the production of geothermal steam, and the separated steam is directed to the turbine/generator set(s). Generally, individual turbine/generator sets are sized **for** approximately 50 megawatts of power production; however, this will vary depending on inlet steam conditions.

The exhaust from the turbine passes through a condenser which produces a condensate stream and a noncondensable gas stream (NCG) stream consisting mainly of carbon dioxide, CO_2, varying amounts of hydrogen sulfide, H_2S, and trace quantities **of** other gases such as nitrogen. This NCG can vary from 1% to **20%** of the inlet stream to the turbine. The condenser can be either a direct contact condenser **as** illustrated in Figure 1 or a surface condenser as illustrated in Figure ***2***. In Figure 1, the cooling tower can be replaced with air-cooled exchangers (fin-fans).

Binary systems are used when processing relatively low temperature geothermal fluids. In addition, they are often used to recover waste heat from the separated brine prior to reinjection. These systems employ a low boiling point, high vapor pressure, secondary fluid to replace steam in the typical Rankine cycle. **As** illustrated in Figure **3**, the secondary fluid is vaporized by indirect heat exchange with the geothermal fluid. The cool, geothermal fluid is reinjected, and the vaporized secondary fluid is expanded across a conventional turbine to produce power. The secondary fluid is condensed in the same manner as steam is condensed in a condensing turbine and is recirculated back to the vaporizer.

The amount and type of hydrogen sulfide abatement required in a geothermal power plant will vary considerably depending on the characteristics of the reservoir(s), the design of the geothermal power plant and the local regulatory requirements. The NCG concentration and the corresponding H_2S concentration can vary dramatically from reservoir to reservoir and from well to well within the same reservoir. Consequently, it is very difficult to establish accurate design bases for the NCG portion of geothermal power plants. Often, a great deal of contingency is included resulting in over-designed NCG systems.

As previously described, the design of geothermal power plants will vary depending upon the classification of the geothermal field. In high enthalpy or vapor dominated fields employing conventional steam turbines, the amount of H_2S contained in the exhaust NCG will depend on the amount of H_2S entering the turbine and the type of condenser employed. In a direct contact condenser as illustrated in Figure *2*, the amount of H_2S which **stays** dissolved in the condensate will depend on how well buffered the cooling water is. The more buffering, the more H_2S which will partition into the condensate. However, any H_2S, which is dissolved in the condensate, will be stripped out in the cooling tower. If a surface condenser is employed as illustrated in Figure 1, more H_2S will partition into the NCG

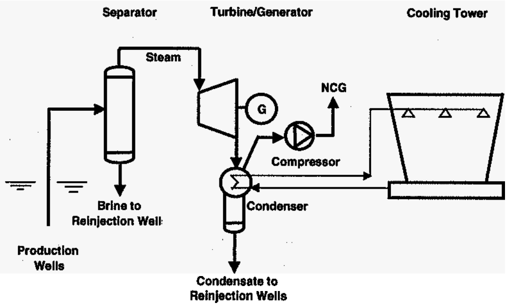

Figure 1 : Geothermal power plant with surface condenser

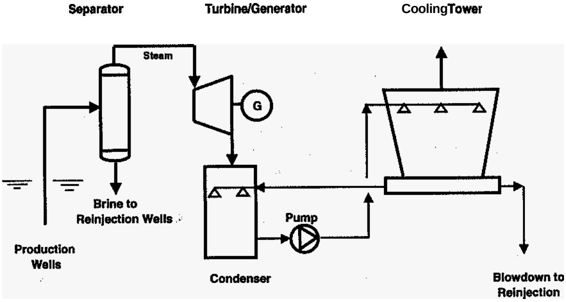

Figure 2 : Geothermal power plant with direct contact condenser

The amount of H_2S, which must he removed, will depend on the environmental, health and safety requirements of the specific area where the geothermal power plant is located. Environmental regulations in the U.S.A. and Europe are very stringent requiring very high removals of H_2S, whereas, the removal requirements are considerably more lenient in some parts of the Pacific Rim. Considerable thought must be given to venting H_2S with cooling tower or fin-fan effluent air since H_2S has a very low odor threshold and is very toxic at low concentrations. And since the exhaust points from these devices are generally not very high, it is conceivable to achieve odorous or even lethal H_2S concentrations at ground level.

2. Hydrogen sulfide removal systems

As described above, H_2S will partition itself between the condensate and the NCG depending on the **type** of geothermal power system employed, particularly, the **type** of condenser employed. Consequently, the type of H_2S removal system employed will depend on the amount of H_2S present and how it partitions between the condensate and the NCG.

21 Removing H_2S from condensate

The easiest method of removing H_2S from condensate is to simply direct the condensate to the cooling tower where the H_2S will **be** stripped from the condensate and be exhausted with the effluent air from the cooling tower. This is a very inexpensive method of disposing of the H_2S; however, as previously stated it may create an odor nuisance or even a hazardous situation. A more safe method of treating the dissolved H_2S (Figure **4)** is to direct the condensate to the cooling tower, but add chelated iron to the cooling water. The chelate or ligand (L) is usually EDTA, ethylene diamine tetraacetic acid, whose only purpose is to increase the solubility of **iron** in water. The iron reacts with the dissolved H_2S as follows.

$$2Fe^{+3}(L) + H_2S \longrightarrow 2Fe^{+2}(L) + S^{o} + 2H^{+} \qquad (A)$$

The ferrous iron (Fe^{+2}) is not capable of reacting with H_2S so it must be reoxidized back to the ferric state (Fe^{+3}) to be reused. This is accomplished when the cooling water is circulated in the cooling tower and comes in contact with air as follows.

$$2\,Fe^{+2}(L) + \tfrac{1}{2}\,O_2 + 2H^{+} \longrightarrow 2\,Fe^{+3}(L) + H_2O \qquad (B)$$

The sulfur, which is formed in Reaction A, is a solid, which if left as is, will eventually plug the cooling water system. To prevent this from happening, a sulfite, usually in the form of sodium sulfite, is added to the cooling water. The sulfite reacts with the sulfur as follows to form a water soluble thiosulfate, which can he reinjected into the geothermal formation.

$$S^{o} + Na_2SO_3 \longrightarrow Na_2S_2O_3 \qquad (C)$$

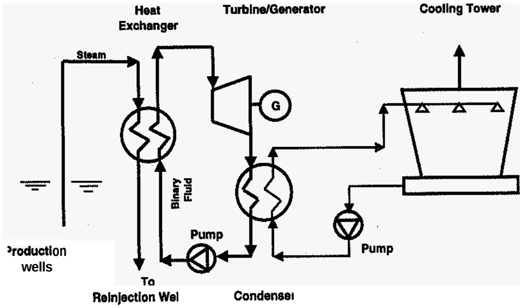

Figure 3 : Geothermal power plant with binary cycle

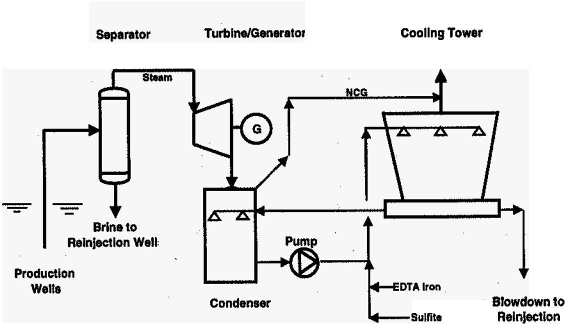

Figure 4 : H_2S removal from condensate

2.2 Removing H_2S from condensate and NCG

If both the condensate and the NCG require H2S removal treatment, the RT-2 Technology (Bedall et al. 1996) licensed by The Dow Chemical Company may be used. In this process (Figure 5), the NCG is processed in a thermal oxidizer where the H_2S is converted to sulfur dioxide, SO_2, as follows;

$$H_2S + 3/2\,O_2 \longrightarrow SO_2 + H_2O \qquad \text{(D)}$$

The hot effluent gas from the oxidizer is then quenched and cooled with an alkaline solution of sodium hydroxide which converts the SO_2 to $SO_3^{=}$ which reacts with the NaOH to form sulfite as follows;

$$H_2O + SO_2 + 2\,NaOH \longrightarrow Na_2SO_3 + 2\,H_2O \qquad \text{(E)}$$

2.3 Removing H_2S from NCG with scavengers

If the amount **of** H_2S to be removed from the NCG on a daily basis is **less** than approximately 140 Kg per day, it is generally economical to employ an H_2S scavenger such as Sulfur-Rite™ manufactured by USFilter /Gas technology products. The Sulfur-Rite system is a fixed bed process consisting of an iron-based material, which reacts with H_2S to form innocuous iron pyrite (Fool's Gold).

$$H_2S + \text{Sulfur-Rite} \longrightarrow H_2O + FeS_2 \qquad \text{(F)}$$

The process is a relatively simple, batch type system consisting of carbon steel vessel(s), which hold the iron-based media. The NCG is passed through the vessel(s) until all of the iron has been converted to pyrite. The vessel is then shutdown, emptied and refilled with fresh media. **A** "Lead-Lag" arrangement (Figure *6)* can be employed which permits continuous treatment of the NCG even during changeouts. In this processing scheme, the NCG **flows** through two Sulfur-Rite vessels in series. When the outlet H_2S concentration in the first vessel is the same as the inlet concentration, the vessel is shut-in, and the media is replaced. During the changeout, the NCG is processed through the second vessel only. When the change out is complete, the flow direction is reversed.

The media is non-regenerable resulting in a high relative operating cost of approximately **$12.00(US)** per Kg of H_2S removed. However, the system is simple and non-corrosive, which results in relatively low capital investments.

The major difficulty involved in using solid-based scavengers in Europe is disposal of the spent material. In other **parts** of the world, the spent material is simply landfilled in non-

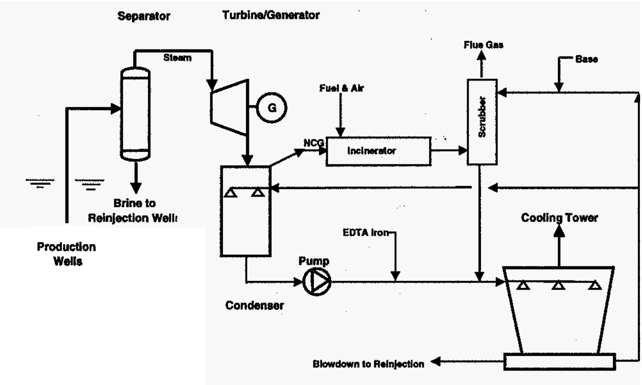

Figure 5 : Dow's RT-2 process

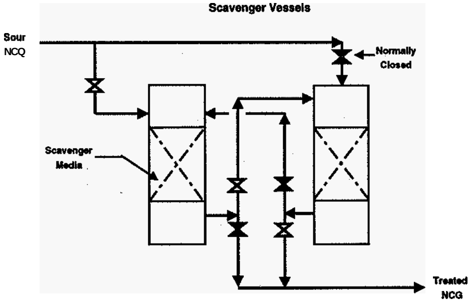

Figure 6 : Lead-lag scavenger system

hazardous facilities. However in Europe, landfilling is discouraged and expensive. Consequently, means of using the material as raw material for bricks, etc. are being investigated.

The solid type scavengers can be replaced with liquid scavengers, which are generally triazine-based. The advantage of liquid-based scavengers is that the spent material can be injected downhole for disposal. The disadvantage of liquid scavengers is that they are very expensive, having a relative cost of approximately $33.00(US) per Kg of H_2S removed.

2.4 Removing H_2S from NCG with liquid redox

Because of their high relative operating costs, H_2S scavengers systems are generally limited to approximately 200 Kg/day of H_2S. Above this amount, liquid redox systems are generally employed to treat NCG because they can achieve very high removal efficiencies (99^+ %) and because they have very high turndown capabilities. The LO-CAT II® process is the most widely used liquid redox system and is considered by some (Mason 1966) to be the best available control technology for geothermal power plants.

The LO-CAT II Process employs a non-toxic, chelated iron catalyst, which accelerates the oxidation reaction (Eq. G), between H_2S and oxygen to form elemental sulfur.

$$H_2S + \tfrac{1}{2} O_2 \longrightarrow S^\circ + H_2O \qquad (G)$$

As implied by its generic name, liquid redox, all of the reactions in the LO-CAT II process occur in the liquid phase in spite of the fact that Equation G is a vapor phase reaction. In the process, the NCG is contacted in an absorber with the aqueous, chelated iron solution where the H_2S is absorbed and ionizes into sulfide and hydrogen ions as follows.

$$H_2S(\text{vapor}) + H_2O \longrightarrow 2H^+ + S^= \qquad (H)$$

The dissolved sulfide ions then react with chelated ferric ions to form elemental sulfur as follows.

$$S^= + 2Fe^{+++} \longrightarrow S^O + 2Fe^{++} \qquad (I)$$

The solution is then contacted with air in an oxidizer where oxygen is absorbed into the solution and converts the ferrous ions back to the active ferric state as follows.

$$\tfrac{1}{2} O_2(\text{vapor}) + H_2O + 2\,Fe^{++} \longrightarrow 2\,Fe^{+++} + 2\,OH \qquad (J)$$

Adding Equations H, J and I yields Equation G.

As illustrated in Figure 7, Autocirculation type LO-CAT units are generally used in geothermal power applications. In this type of unit, the absorber and oxidizer are contained in one vessel and separated by baffles. Due to the large differences in aerated densities between the liquids in the absorber and the oxidizer, large circulation rates are achieved between the various compartments of the vessel without having to employ pumps. The

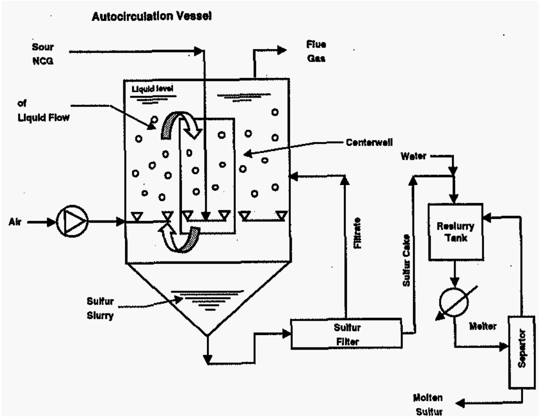

Figure 7 :LO-CAT autocirculation process

NCG enters the absorber section of the vessel where it is contacted with oxidized LO-CAT solution and where the H_2S is converted to elemental sulfur. The partially reduced solution then circulates to the oxidizer section where it is contacted with air, which reoxidizes the iron. The exhaust air from the oxidizer and the sweet NCG from the absorber are exhausted to the atmosphere.

In the conical portion of the vessel, the sulfur will settle into a slurry of approximately 15 wt%. A small stream is withdrawn from the cone and sent to a vacuum belt filter where the sulfur is further concentrated to approximately 65 wt% sulfur. Some units stop at this stage and sell the sulfur cake as a fertilizer. If molten sulfur is required, the cake is reslurried and melted as shown in Figure 7.

Although liquid redox systems are relatively expensive to install compared to a scavenger system, they are very inexpensive to operate. Operating costs usually range between $0.20/Kg of H_2S to $0.25/Kg of H_2S.

3. summary

Although geothermal power plants are environmentally attractive because of their renewable energy status, they do propose an environmental threat because of the hydrogen sulfide, H_2S, which is contained in most geothermal steam sources. Depending on the type of condenser employed the H_2S will partition itself in various ratios between the condensate and the noncondensable gas (NCG). In most populated areas, this H_2S must be removed from the noncondensable gas (NCG) streams prior to exhausting the NCG to atmosphere, and the optimum type of process for removing the H_2S depends on the amount of H_2S in the NCG.

References

Bedall S.A., Hammond C.A., Kirby L.H. & Oostwouder S.P. 1996. H2S Abatement in geothermal power plants. Released at the Geothermal Resources Council, 1996.

Mason T.R., 1966. CalEnergy's Coso Operation: A substantial commitment to the environment pays off, Geothermal Resources Council Bulletin, lune, 1996 : 233-235.