Geothermal Ammonia Emissions Effect on Fine Particulate Formation

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ABSTRACT

A review of the evidence presented during development of the Salton Sea Unit 6 Geothermal Project with regard to ammonia's role in PM-10 formation and a discussion of the implications this presents for future geothermal projects.

Introduction

The presence of ammonia in geothermal fluids has been known since the industry's early stages. For those facilities and projects that utilize the geothermal condensate fluids in a cooling tower, or reuse the condensate, the ammonia present can be released to the air. Because of the low concentrations, low toxicity, and minimal air quality impact, ammonia emissions have not historically triggered a closer examination as an environmental air issue. However, since the start of PM-2.5 (very fine particulate matter with mass median aerodynamic diameter less than 2.5 micrometers (μm)) ambient monitoring, the role of ammonia emissions in very fine particulate formation has been under extensive review because ammonia nitrate is usually a major component of PM-2.5 and consequently PM-10. The Salton Sea Unit 6 Project (Unit 6) was the first major geothermal project to undergo a review from the California Energy Commission (CEC) with particular emphasis on whether or not there would be particulate formation resulting from ammonia emissions in an area rich in ammonia. The CEC determined that "while CEC staff has presented a credible, hypothetical case that under certain circumstances of ammonia-lean, high relative humidity, and low temperature conditions that some ammonia may contribute to particulate formation in a chemical reaction that is also reversible, for purposes of CEQA, the CEC needs more than a mere possibility that this chemical reaction might take place as a result of project operations in a way that could contribute to PM-10 violations and thus create a significant impact". The Commission amended a Condition of Certification by which the Applicant would have been required to routinely investigate advances in ammonia control technology and report to the Commission, also no significant impact resulting from ammonia emissions was determined. This paper reviews the data presented by the CEC staff and the Applicant with regard to ammonia emissions and discusses potential implications for future geothermal projects.

PM-2.5 Background

U.S. Environmental Protection Agency (EPA) issued new national ambient air quality standards for very fine particulate, PM-2.5, in 1997. The State of California adopted fine particulate standards in 2003. One of the interesting aspects of very fine particulate is that it is generated primarily as a secondary pollutant. The gases significant to formation are the acid gases, nitrogen oxides, sulfur dioxide, and ammonia. Studies have shown that nitrogen oxides can form nitrate and subsequently combine with ammonia to generate fine particulate ammonia nitrate in a polluted environment at a rate of 10 to 30 percent per hour. While the emissions of nitrogen oxides have been regulated by the air agencies for some time, ammonia emissions have not. In fact, there are still a lack of data and significant gaps in knowledge regarding natural and anthropogenic ammonia emissions. EPA and the California Air Resources Board (CARB) have both been preparing inventories of ammonia emissions sources because of the non-attainment of the federal and state fine particulate standards in many areas of California and the United States. Two areas, Denver, Colorado and the San Joaquin Valley in California have conducted extensive studies to understand the complex aspects of fine particulate formation. The chemistry of the reactions is complex, and dependent upon such factors as concentration, humidity and temperature. High humidity and low temperatures favor the generation of fine particulate.

Sulfur dioxide also plays a role similar to nitrogen oxides, except that in the western United States sulfur dioxide emissions are a minor part of total acid gases. In the eastern United States the roles are reversed and sulfur dioxide is normally the significant contributor to fine particulate formation.

Salton Sea Unit 6 Project Emissions

The composition of the geothermal brine for use at the Salton Sea Unit 6 Project was estimated to contain approximately 59 parts per million (ppm) of ammonia (NH_3) and 359 ppm of ammonium ion ($NH4^+$). In flashing the brine, the ammonia and hydrogen sulfide would follow the steam and when the steam was condensed, almost all of the ammonia and approximately 20 percent of the hydrogen sulfide would partition to the condensate. Insignificant amounts of ammonia are normally carried with the non-condensable gases. The condensate was then sent to an abatement unit to convert the hydrogen sulfide present to a sulfate through the use of biofiltration. With the resultant change in pH, the ammonia was expected to off-gas as it cycled through the cooling tower. The Project's ammonia emissions were estimated to be over 2,700 tons per year.

Discussion

The Applicant, in its initial application noted, "…in general terms, the significance of ammonia emissions with regard to particulate conversion is dependent upon the chemical makeup of the local air quality. Ammonia emissions in a highly acidic (ammonia lean) environment can potentially produce particulate matter, while ammonia emissions in a basic (ammonia rich) environment can potentially produce no additional particulate." (CE Obsidian Energy, LLC, Salton Sea Unit #6 Project, 02-AFC-2, Data Request Response Set 1) "While there is limited data available regarding the chemical makeup of the air quality surrounding the Salton Sea Unit 6 Project, the local area is expected to be ammonia rich. The reasons include: 1) Rural areas of California are considered ammonia rich, 2) The other Salton Sea geothermal facilities also emit ammonia, 3) The area surrounding the facility is cultivated and anhydrous ammonia is routinely applied to the fields two to three times per year, 4) Located in the area (four mile radius) is a cattle feed lot, which contributes ammonia emissions to the local environment. Based on this information, the Applicant does not believe the addition of ammonia from the Salton Sea Unit 6 Project would contribute to additional particulate formation." (CE Obsidian Energy, LLC Salton Sea Unit #6 Project, 02-AFC-2, Data Request Response Set 1)

The CEC staff suggested that the Applicant neglected the transport of pollutants from the surrounding air basins (South Coast, San Diego and Mexico) and that these emissions were not likely to be ammonia rich. Staff additionally noted that while reviewing of the nitrate/sulfate particulate mole ratios between Imperial County and San Joaquin Valley (an area acknowledged as ammonia rich by the CEC staff), the data indicated to them that Imperial County may not be ammonia rich. Therefore, to be conservative, the CEC staff assumed the area to be ammonia lean, and consequently the ammonia emissions did have the potential to create significant secondary particulate impacts.

In addition, CEC staff believed that the formation reaction was reversible and that as more reactants are added the higher concentrations would push the reaction. Thus, even if the area was considered ammonia rich, staff expected additional particulate formation. Staff could not calculate the expected amount of particulate generated, and as a result provided a table of potential generation rates. A one percent conversion rate (27.0 tons of ammonia) was expected to generate approximately 100 tons of particulate. If all of the ammonia converted, it would amount to over 10,000 tons of particulate.

Imperial County is classified as a desert climate with low precipitation, hot summers, mild winters and low humidity. Ammonia nitrate particulate is primarily generated at temperatures below 15 ºC (59 ºF). Above 35 ºC (95 ºF) the gaseous phase is favored. Thus, particulate ammonia nitrate is generated under conditions of high relative humidity and low temperature. The mean annual temperature at the nearest station (Brawley) is 72.4 ºF and average relative humidity for the County is 25 percent. These conditions are not conducive to ammonia nitrate particulate formation.

Area-wide emissions data for the surrounding air basins were also presented to the CEC staff and is listed in Table 1.

Table 1. Area-wide emissions data for the surrounding air basins.

Air Basin		NO_2	SO_2	Ammonia	Mole Ratio
Imperial County	(tpd)	33.5	0.94	50+ (a)	3.87
	(mole tpd)	0.73	0.015	2.94	
San Joaquin Valley	(tpd)	525	34.5	369 (b)	1.74
	(mole tpd)	11.4	0.54	21.7	
San Diego County	(tpd)	220.5	7.51	NA	NA
	(mole tpd)	4.79	0.12		
South Coast	(tpd)	1088	64.5	182 (b)	0.42
	(mole tpd)	23.7	1.0	10.7	
Mexicali (c)	(tpd)	55.9	11.4	23.5	1.10
	(mole tpd)	1.22	0.18	1.38	

(a) Current Imperial County APCD estimate taken from its PDOC
(b) Year = 2000
(c) Year = 1996 (Source: Air Emissions Inventory for Mexicali, Baja California – Radian International)
tpd = tons per day
NA = Not Available

Based on the table, the Applicant stated that, Imperial County, Mexicali and San Joaquin Valley were ammonia rich, and the table showed that SO_2 plays a minor role in potential total particulate formation, with NO_2 providing 85% to 97% of the acid gases on a mole ratio basis. NO_2 is the major factor in secondary particulate generation for these areas.

Long-distance transport of nitric acid was not expected since NO_2 oxidizes quickly to nitric acid and nitric acid fairly rapidly deposits out. Thus, San Diego and South Coast emissions were not expected to significantly influence Imperial County air quality with regard to secondary ammonia nitrate formation, while Mexicali, because it was located nearby could potentially have an impact. However, even including Mexicali's emissions, the project area would still be very ammonia rich with a combined mole ratio of 1.85. Mexicali ammonia emissions did not include motor vehicles and natural sources. In San Joaquin Valley, these sources contributed five percent to the total, while in the South Coast these sources contributed thirty-seven percent of the total ammonia emissions. Thus, the 1.85 mole ratio was an understatement for the combined Imperial County and Mexicali area. Therefore, the data showed Imperial County was ammonia rich even when transported emissions were taken into consideration.

Regarding the issue that Imperial County was not ammonia rich because the ammonia to nitrate/sulfate particulate mole ratio in San Joaquin Valley was almost twice that of Imperial County, the Applicant noted the ratio, as presented by staff, could not provide any information regarding whether an area is ammonia rich or ammonia lean because the data did not contain information on the available concentrations of ammonia/nitrate/sulfate and other factors. Further, the recent study in Denver found no such correlation (Watson, J. G., Northern Front Range Air Quality Study).

It was the CEC staff's opinion that regardless of the area's ammonia status (rich or lean), there could still be some additional reaction and particulate formation as a result of the additional ammonia emissions. The Applicant responded that the Northern Front Range Air Quality Study showed that this was not the case in an ammonia rich environment such as Imperial County. Figure 8.2-8 of that report illustrates changes in particulate nitrate concentrations in response to changes in ammonia on pages 8-13 of that study. Increases in ammonia concentrations did not lead to increases in particulate nitrate concentrations. To provide staff with greater confidence in these results, calls were made to the Project Manager of the Northern Front Range Air Quality Study, to the California Air Resources Board staff, and to the San Joaquin Valley Air Pollution Control District staff to review the issue. Each of these agencies confirmed that in rich ammonia environments, changes in ammonia concentrations did not effect particulate formation. CARB staff also felt it should be clear that the equilibrium equation was between particulate and nitrogen oxides, not between particulate and ammonia.

Conclusion

After reviewing the data presented by the CEC staff and the Applicant, the CEC commissioners concurred that the Salton Sea Unit 6 Project would not contribute to the formation of fine particulate matter in an environmentally significant way. Experience with the Salton Sea Unit 6 Project shows that future geothermal projects releasing ammonia to the environment will need to review the role of ammonia emissions in the formation of PM-2.5/PM-10, especially those proposed for ammonia lean areas. Even in ammonia rich areas, project reviewers will need to assess the current understanding of PM-2.5 formation. Since ammonia is now connected indirectly to the PM-2.5/PM-10 ambient air quality standards, the Geothermal Industry can expect further discussions on this issue.

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