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The Role of Ammonia at the Coso Geothermal Field

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ABSTRACT

Vapor phase ammonia results have been produced from the Coso Geothermal Field for over 20 years with no large increase in concentration. After the steam turbine all of the ammonia partitions into liquid condensate that goes to the Cooling Towers which concentrates the ammonia through evaporation from 3 ppm in produced steam to 10 ppm in winter and 45 ppm in summer in the cooling tower. All the other geothermal gases CO2, H2S, H2, CH4, N2, and Ar partition into the vapor phase. Very little of the H2S partitions into the condensate or liquid phase compared to other geothermal power plants. The cooling tower blowdown is injected back into the resource were small differences in ammonia concentration can be monitored in the steam produced. These are plotted to show returns of injection. In the Navy I area of Coso the wells are mostly dry steam wells where these plots have been the most useful. Other areas of Coso have wells with both brine and steam phases and the condensate is mixed with brine before injection and the Ammonia changes are not as pronounced. The vapor phase ammonia is in equilibrium the ammonia in the brine. Ammonia is not measured in the brine and is calculated form equations by Fournier and Giggenbach. The highest concentrations of ammonia in steam are 20 ppm in three wells that are near a hot spot with a magmatic signature. This is a NH4Cl species similar to the Northwest Geysers but at a lower level. Upon completion of drilling Prati State 10 had the highest dry gas ammonia concentration at 10%. Coso wells are much lower at less than 0.5 percent After years of injecting all of the ammonia produced back into the resource the ammonia concentrations in produced steam have not increased.

1. INTRODUCTION

The Coso Geothermal Field has several different reservoir types such as 100 percent steam wells from shallow a steam cap, additional types are two-phase wells with a high steam fraction at BLM West and the two-phase wells with a low steam fraction in the East Flank area, none of these areas has excessive concentrations of ammonia. The Volcanic field and associated production fluid from it are generally below 5 ppm in steam. Ammonia is routinely measured as part of the Non condensable gas analysis for over 20 years. Other gases analyzed are CO2, H2S, CH4, N2, Ar, and H2. All these gases do not drop out into the condensate after going through the steam turbine and condenser they go into the off gas. The ammonia is different and partitions completely into the liquid condensate. This condensate goes to the cooling tower where the ammonia concentrates proportional to the amount of evaporation in the cooling towers. Initial concentrations in the hotwell condensate are 2-4 ppm and concentrate in the cooling tower to just below 10 ppm in the winter and to around 45 ppm in the summer, see Figure 1. The difference in evaporation from winter to summer concentrates the ammonia to different concentrations. All of the condensate is reinjected into the reservoir and can be tracked in several cases as it returns in the steam of the production wells. Beale, (1993) used this method as a natural tracer in the Geysers. Well 77-7 has a strong correlation with an increase in produced ammonia and an isotopic shift that is associated with injection recovery, see Figure 4 and 5.

2. MONITORING

Cooling Tower samples are collected quarterly with NH3 concentrations varying from 3 to 100 ppm. Higher concentrations are associated with the higher evaporation rates during summer operations, the winter concentrations are lower with the lower evaporation rate. The cooling tower cycles up 2 to 4 times based upon the evaporation rate, and is calculated by the difference in dissolved chemical concentrations measured between the hotwell condensate and the cooling tower. All of the ammonia in the steam that goes through the turbine and then the condenser is partitioned into the condensate that is the makeup water for the cooling towers. The cooling tower water is then injected back into the reservoir. The other gases CO2, H2S, N2, Ar, and H2 do not condense and partition into the vapor phase and are extracted from the condenser by a steam jet and vacuum pump. At Coso very little of the H2S partitions into the condensate compared to other Geothermal Power Plants, if the ammonia concentration was higher it would change the condenser pH and more H2S would partition into the condensate. As soon the NH3 condenses the NH3 converts to the Ammonium Species, the NH3 is kept as the unit to compare to the steam phase analysis.

For eight years 2009 to 2017 ground water from Rose Valley Hay Ranch fluid was used as augmentation water to recharge the reservoir. This water source has no NH3. When used in the cooling towers in mid-summer it dilutes the ammonia that is higher in concentration from the higher evaporation rate. Augmentation or Hay Ranch fluid is used now only in the summer time as make up water on a limited time basis.

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Ammonia in steam does not vary as much in the produced steam xompared to the cooling towers unless the NH3 from the reinjection of the cooling tower fluids is mixed with the produced steam. Wells such as 77-7 over time have a slow increase in ammonia concentration from recovered reinjected fluid. At the same time well 52-7 does not show an increase with time. Both the increase and the decrease is in the two wells around 1 ppm higher and 1 ppm lower, see Figure 2 and 4.

3. MAGMATIC INFLUENCE

The highest concentrations of ammonia measured in the field are associated with a "hot spot" in the south west part of the Coso Field. The ammonia in the highest concentrations is attached to chloride as NH_4Cl similar to the Northwest Geysers HTR steam system but to a lesser extent. Initial ammonia concentrations in wells in the Northwest Geysers were has high 10% on dry gas volume basis. At Coso they are less than 0.5% dry gas basis. Initial concentrations at Coso are a factor of 10 lower than the Northwest Geysers initial conditions. How much this area at Coso contributes to adding ammonia to the total fluid in the reservoir is small because it is only in a few wells. These few wells can have over 80 Degrees of superheat and have a higher rate of corrosion. These are dry wells that are adjacent to two-phase wells with excess steam and high steam fractions, flashing into the reservoir can be over 20 percent. The ammonia in these three wells also have elevated chloride concentrations that are associated with higher corrosion rates with the dominate species as hydrochloric acid, the ammonia is part of this, but some of it coming from the injection fluid too. Returns from injection have the strongest effect and the highest returns of volatile chloride and ammonia. The effects of "Dew Point Corrosion" first described by Hirtz (1989), see Figure 6, where mitigated using an inhibitor that created a dry coating on the inside of the pipe line. The inhibitor does not work for two-phase wells or dry steam wells near saturation. In contrast other Geothermal Areas use a wet based method with caustic soda and liquid separators to neutralize the steam and carry the chlorides out of the steam. At Coso any liquid would wash coating off the pipe line and leave the pipe exposed to corrosive chlorides, so the wells have to be superheated for this method to work. This method is no longer used at Coso because there is no injection in this area of the field and there is much less corrosion coming from injection returns.

Initial steam samples from the Northwest Geysers showed a shift stable isotopic that was stronger than other parts of the main field. The amount of shift helped define the HTR part of the field. Similarly at Coso the strongest isotopic shift is in these three wells and in this part of the field, this helps define the magmatic influence in the southwest area of the field. The shift in stable isotopes at Coso is not as much as the North West Geysers.

4. MODELING AND PH

The equilibrium of ammonia in the reservoir and distribution into the vapor phase has a dependence on the reservoir temperature and pH, For Ammonia concentrations in the vapor phase to be as steady as they have been for over 20 years a steady source of ammonia in the reservoir has to be stable. Acidification of the reservoir for scale control has not changed the equilibrium in the reservoir that much. Modeling using Watch estimates the amount of ammonia that would be retained in the brine is less than 1 ppm. Ammonia is not measured in the brine but calculated by using the gas distribution coefficient B developed by Giggenbach (1980). Concentrations in the brine are too low to measure with Coso lab equipment there is an interference that the condensate does not have. Early work by Fournier provides equations that include pH and temperature to estimate the amount of ammonia dissolved in the brine or condensate. There is just not enough ammonia to raise the pH in the brine or condensate, even with all the ammonia returned to the reservoir the pH and redox remain stable. For a resource that has large differences in flash fraction between wells the chemistry stays stable for the most part. Ammonia increase are more from injection breakthrough or reservoir temperature rather than high evaporation or high flash fractions.

5. GEOTHERMOMETRY

Even though ammonia is considered to be enriched at Coso it is lower than initial concentrations in the Geysers by a factor of 10. Initial concentrations in steam at Coso are typically not above 5 ppm and stay in a narrow range close to the initial levels for over 20 years, see Figure 1 and 2. All of the ammonia produced at Coso has been returned to the reservoir at a higher concentration than what is produced. Yet concentrations of ammonia do not increase in produced steam over time except for wells that have direct breakthrough such as 77-7. The ammonia geothermometer is independent of redox state. The reservoir is considered slightly reduced. Cooling Tower fluids are fully oxygenated and carry the ammonia back into the reservoir. Initial state geothermometer work by Geologica show the highest temperatures in the south west corner, were the "hot spot" is located see Diagram 5. A review of geothermommeters by Powell(2000) has the NAH geothermometer not widely used because of near surface ammonia and a sensitivity to hydrogen. The south west part of Coso has the highest concentrations of hydrogen, plus the ground water based Hay Ranch augmentation fluid that was injected does not have any ammonia in it.

6. CONCLUSION

With all the ammonia returned to the reservoir over time there is not a build-up or large increase in concentration in the produced steam. An over-all semi equilibrium exists that is based on reservoir temperature. Modeling of pH changes so far has not made as much of a difference compared to reservoir temperature in predicting changes in partitioning of ammonia between steam and brine. The reservoir is hot enough to create a vapor phase in the reservoir at depth that moves any ammonia in the liquid phase into the vapor phase. Injection rates back into the resource are large at times up to 800,000 pounds per hour in single well in the winter that mixes the cold fluids with brine and steam. In the steam cap it for sure mixes with a large number of wells but rarely kills them. Wells such as 52-7 have reduction of non-condensable gas produced in the winter when there is more liquid available to inject, see Figure 3. But the ammonia stays relatively constant in this well, see Figure 2. As the injection fluid moves through the reservoir it is more than likely that just a small portion of the injection interacts with producing steam before flowing down to a lower part of the reservoir. Coso does not have defined bottom to the reservoir. Often reservoir modeling programs have to extend the estimated bottom of the resource for better history matches. A well in the steam cap that produces from a shallow depth can have a similar ammonia concentration compared with a well flowing from 9000 feet on the East Flank. Access to production fluids is through a fracture based system that produces fluids from depths of 10,000 feet for so,e wells. The steam fraction can change the enthalpy can change but the ammonia concentrations remain similar pointing to a common source that may be deeper than the wells. The reservoir may be larger than we think, vertically.

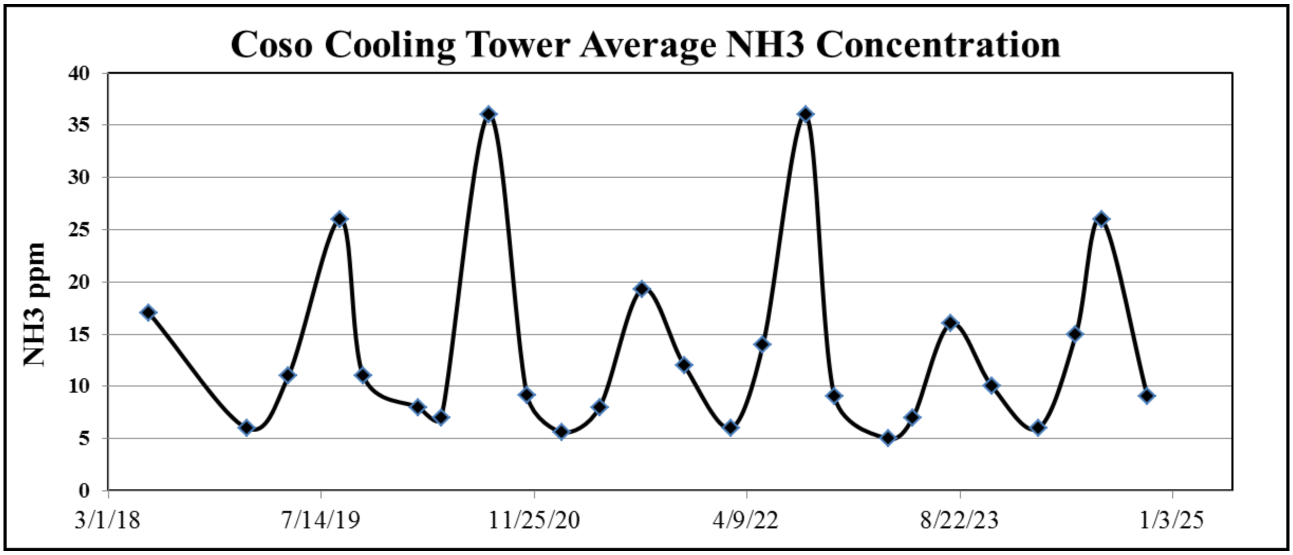

Figure 1: Average Cooling Tower Ammonia concentration of all Towers. In Summer One Individual Tower has NH3 concentrations above 100 ppm.

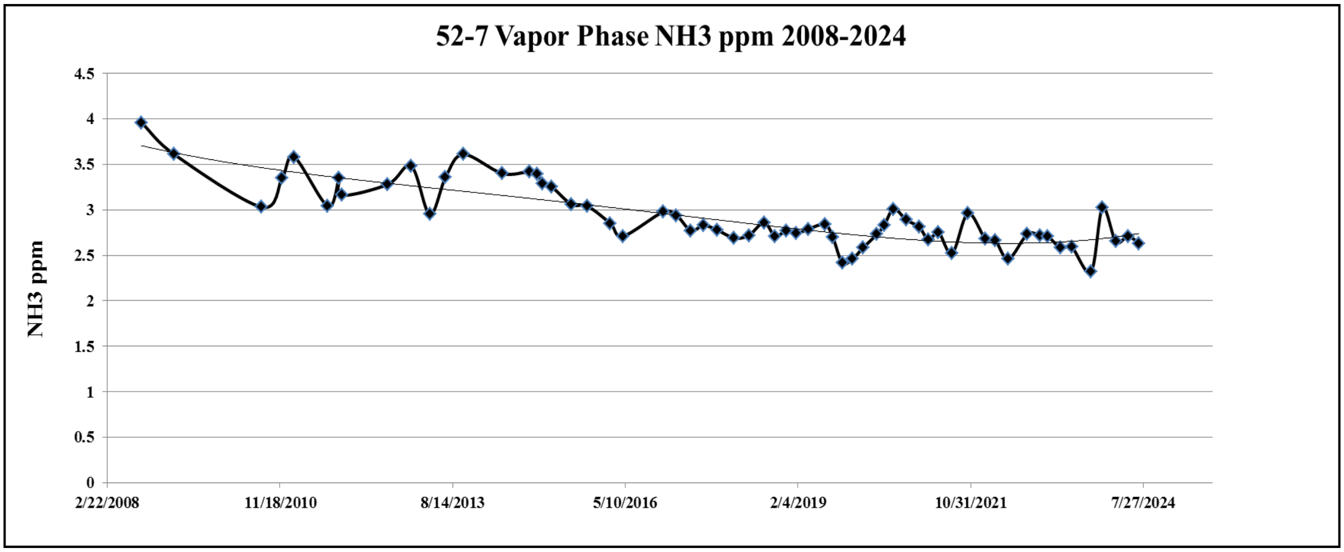

Figure 2: Ammonia concentrations for Well 52-7 steady but with small variations.

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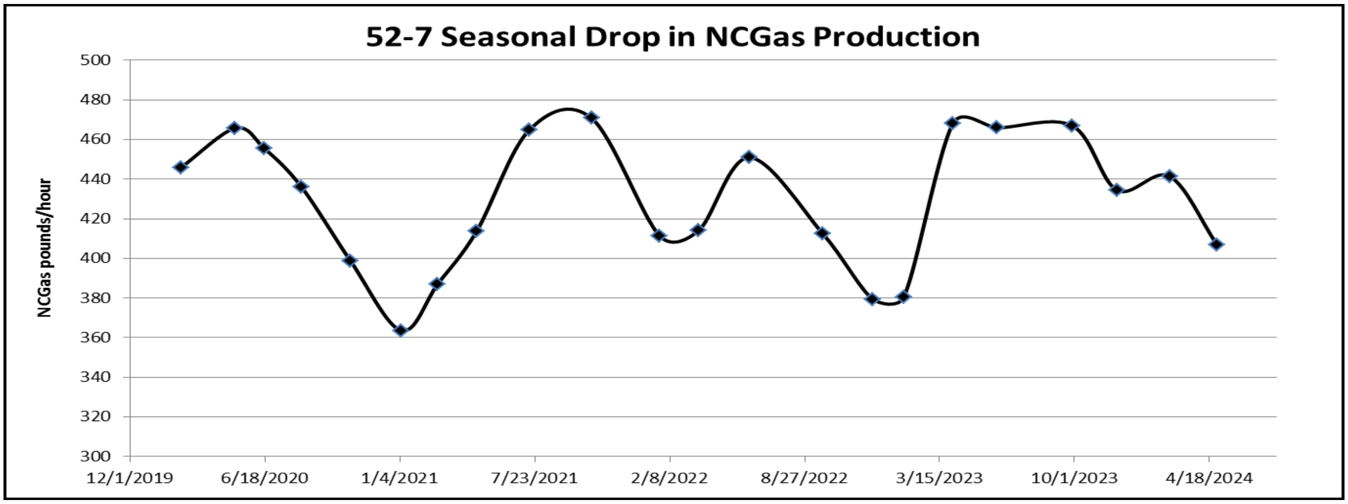

Figure 3:Seasonal Change in Total NCGas for Well 52-7 is much larger than the Variation in Ammonia in Figure 2.

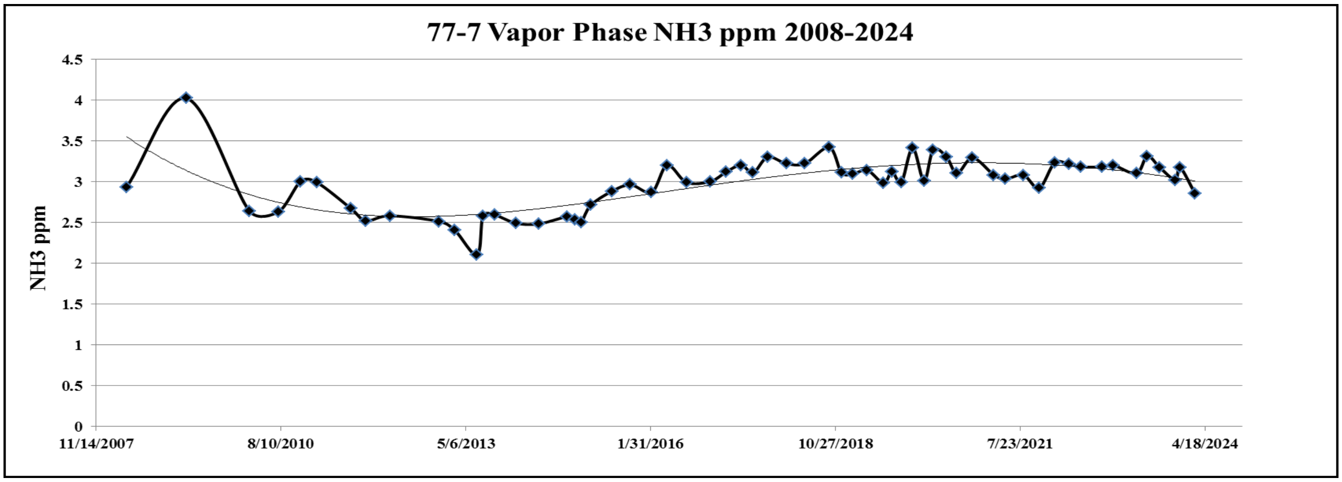

Figure 4: Slow Ammonia increase in Well 77-7 showing Injection Recovery over Time.

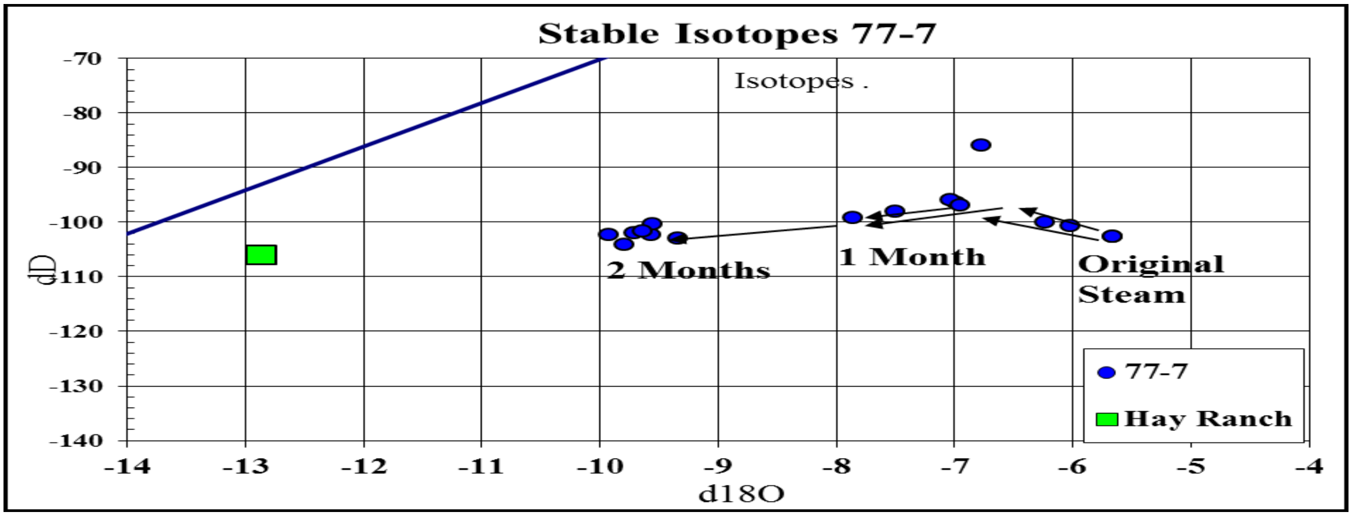

Figure 5: Stable Isotope Response to Injection in Well 77-7 in 2011.

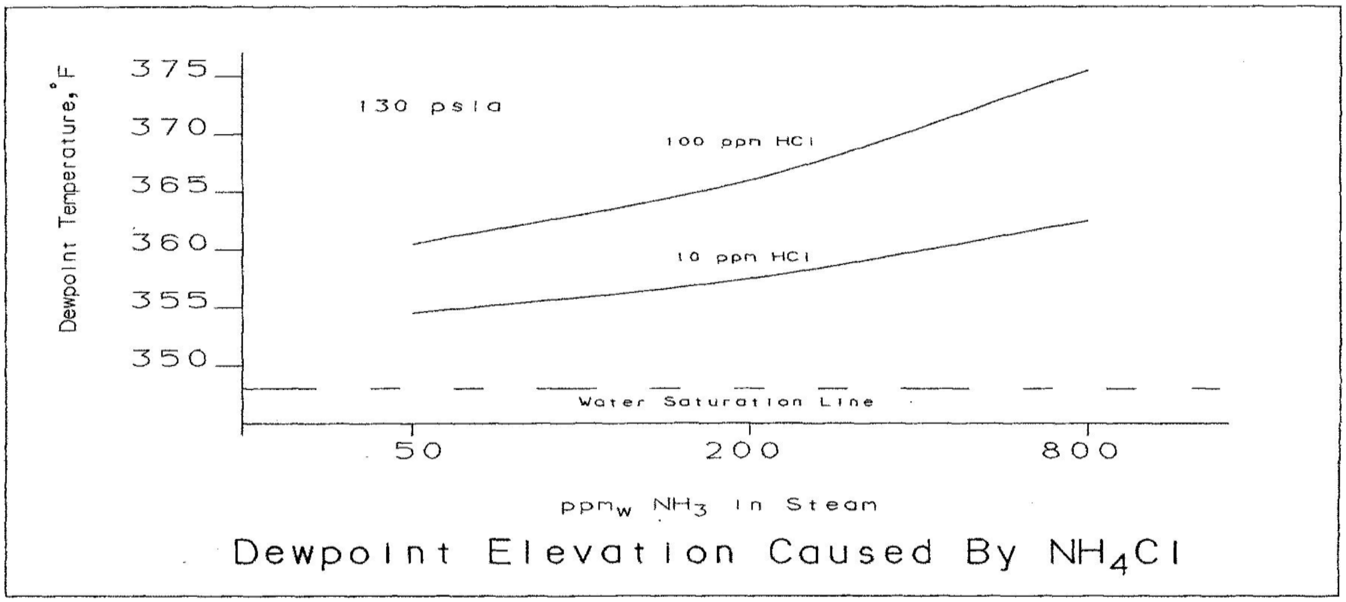

Figure 6: Diagram from Hirtz (1991) showing the effects of even small amounts of Ammonium Chloride on the Dewpoint Temperature.

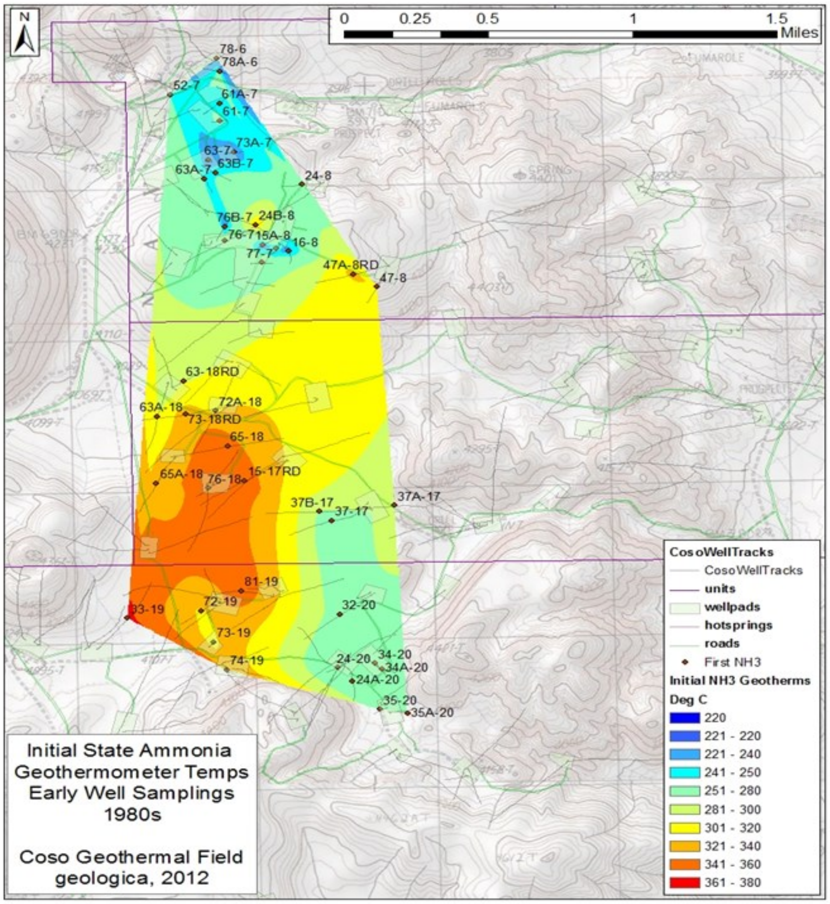

Figure 7: Initial State Ammonia Geothermometer, Showing the higher Temperatures in the South West part of Coso. This is also were the higher concentrations of Ammonia in steam are located.

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