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NITROGEN CHEMISTRY IN COOLING TOWER WATER AT MAGMA POWER
COMPANY'S FOUR SALTON SEA KGRA POWER PLANTS

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ABSTRACT

Magma Power Company operates four geothermal flash plants in the Imperial Valley of California at the Salton Sea KGRA. The first plant began successful production in late 1985, and the rest in the late 1980s. The cooling towers at each of the four plants have developed similar chemistries since operation began that is unique due to the practice of using geothermal steam condensate containing dissolved gases and minerals as the prime make-up source to the basin water. The main concern and research emphasis of the cooling tower water has been concentrated on how to best control the nitrogen chemistry, specifically, the appearance and departure of the nitrite (NO₂⁻) and nitrate (NO₃⁻) ions. The source of these two species is the oxidation of ammonia (NH₃), which enters the cooling water system via two geothermal condensate make-up water streams. If the oxidation mechanism is left unchecked, the tower water pH will fall below 6.0, resulting in unacceptably high generalized corrosion rates.

INTRODUCTION

The use of condensed geothermal steam has produced perplexing water chemistry at the four Magma plants. The first, the Vulcan Power Plant (38 MW) began production in late 1985, the Del Ranch Plant (42 MW) and the J.J. Elmore Plant (42 MW) in late 1988, and the J.M. Leathers Power Plant (42 MW) in late 1989. Ammonia is provided to the cooling tower water systems with the make-up water but it is oxidized to nitrite then nitrate by inexplicable mechanisms, resulting in pH depression and corrosion. The towers are essentially a NH₃-CO₃ buffer operating between a 7.0 - 8.0 pH range until nitrite/nitrate chemistry begins to appear. The routes to NO₂⁻/NO₃⁻ are believed to be microbiological but the production has not been controlled with the use of general biocides. A chemical route is unknown but with the ineffectiveness of biocides, it has not been ruled out.

The local Imperial Valley region has been intensely cultivated over the last 40 years with ammonia and nitrate added to the soil as fertilizer. A hospitable climate of warm desert days and nights combined with a warm water bath operating at a favorable pH containing plenty of ammonia and oxygen is an ideal place for

nitrifying bacteria to live. Many ammonia plants and refineries have experienced nitrifying bacteria but they are considered by them relatively easy to control; however, many major cooling tower water treatment companies have been retained at various times over the past seven years to research effective control methods for the appearance of the nitrite and nitrate and they have used corporate resources, but they have logged slow progress. This paper describes the origins of the problem, the make-up water, treatment attempts, and the progress that has been made.

Origins

The beginnings of all four of the Magma Power plants cooling tower chemistries are similar. The tower water began with the initial supply of local utility water as it is the only water source available before steam production and condensation. As the plants have come up to full power production, two geothermal steam condensate make-up sources are gradually introduced to the basin, eventually establishing a pH of roughly 7.5 in the water with NH₃ levels of 200 - 400 ppm, and no nitrite or nitrate. In anywhere from hours to a month, nitrite concentrations begin to build. Initially seen at less than five ppm for a day or so, the NO₂⁻ concentration can then rapidly escalate to a few hundred ppm in less than a week.

At first, the NO₂⁻ concentration predominates over the nitrate. Though expensive, chemical treatment with carbamate biocide can control the nitrite level and prevent pH depression. After roughly two years,, a change occurs where the nitrate species begins to predominate with minimal NO₂⁻ levels present. The pH drops to levels of 6.0 - 6.5 and chemical treatment then focuses on pH elevation back up to a comfortable range. While costs to maintain a comfortable pH range are lower, the corrosion rate and mitigation costs are higher. The make-up water chemistry is discussed next.

MAKE-UP WATER

The make-up water to the towers consist of three distinct sources. The main and most consistent source also has the worst chemistry - it is a the steam condensate produced from the first brine/steam separation at approximately 300 psig.

This first flash contains most of the dissolved acid gases and some minerals coming in from the production wells. The condensed sour steam enters the basin flashing over 140 °F and containing 100 ppm H₂S, 270 ppm NH₃, CO₂, and 1-2 ppm Cl⁻ ion. It is the largest contributor of ammonia to the basin chemistry and the apparent source of the nitrite/nitrate levels, even though they have not been found in the make-up stream. Control efforts have been centered on the stream.

An obvious method to control nitrite levels is to eliminate the sour condensate entirely from the cooling water system as a source of make-up water, but this has not been practical. It is incompatible mixing with the injection brine, even after steam stripping, as it reacts to precipitate undesirable solids in the filter cake by-product. Modifying the sour condensate to be compatible with the injection brine is being researched, but even if a compatible method is found, the extra injection flow resulting from the significant sour condensate addition can push the injection system to its limits.

Currently, the sour condensate flow is sent exclusively to the tower basin as it does not have a more appropriate place to flow. Attempts at steam stripping it before combining with the basin water have removed all the H₂S and half of the NH₃ but this has not significantly altered tower water chemistry, and, as mentioned, does not allow mixing with injection fluid.

Another constant make-up source to tower water is the condensed turbine steam collected in the hotwell. This stream is considerably cleaner than the sour condensate and is referred to as hotwell condensate. It contains less than ten ppm of H₂S and roughly 100 ppm of NH₃ at a pH of 9.0. This source contributes less than one-half of the make-up water compared to what the sour condensate contributes.

The local water utility is the third option available to the plants for a make-up water source. The Imperial Irrigation District (I.I.D.) flows Colorado River water to the agriculturally rich valley via a canal system. While this source is considered easier to treat, the other two streams must otherwise be disposed of if not sent to the tower and mixing them with the injection brine is not preferred. This imported water would also have to be paid for, and since the plant's condensate supply compared to its needs is more than adequate with the exception of the hottest summer days, this make-up source is not widely used.

It is believed a tower chemistry made up exclusively of hotwell condensate and local utility water could be low enough in ammonia levels to control nitrite levels as evidenced at one plant temporarily when the sour condensate was removed for a period of days, but a longer trial is certainly needed. During another trial period, the nitrite production was still excessive when the sour condensate make-up was steam stripped and ammonia levels in the basin water were down to 112

ppm, but that was the lowest obtained so the maximum ammonia level without nitrite production is still unknown.

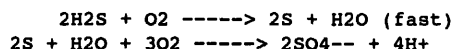
Modifying the Make-Up Water Streams

Attempts at treating the make-up water to control nitrite production have not been entirely successful. The canal water has been halogenated with sodium hypochlorite, alone and in conjunction with sodium bromide producing sodium hypobromite to sterilize the streams. It was postulated that the nitrifiers entered via this water but no strong correlation exists between the use of I.I.D. utility water in the tower and nitrite production.

Both steam condensate make-up streams have also been treated in the plants before being introduced to the tower water in an attempt to remove ammonia to control nitrite/nitrate production. Aeration and steam stripping have both been tried. Steam stripping was the most effective, removing most of the hydrogen sulfide and half of the ammonia in the sour condensate. While this process is the effective in lowering typical operating ranges of the nitrogen species in the tower water, it barely slowed the nitrite production, let alone controlled the problem.

The Presence of H₂S In Make-up Water Streams

Complicating the research of the nitrifying problem further is the additional factor that the presence of H₂S in the make-up water contributes. Ironically, when the pH depression first began to appear in 1986 at the Vulcan plant, it was H₂S that was thought to be the culprit according to either the proposed mechanism:



or due to the presence of thiobacilli organisms which consume the H₂S and produce SO₄⁻⁻. Though H₂S has not been detected in the basin, sulfate ion is found in the water at levels of 200 - 1000 ppm and occasionally, elemental sulfur is deposited in small quantities. It is believed the sulfur species present are from oxidized H₂S entering in the make-up streams, though how it interacts with the oxidation of ammonia is not known.

BLOWDOWN AND EVAPORATION

Cooling tower water leaves the system by either blowdown into a separate injection system or by evaporation to the atmosphere. The rate of cooling tower blowdown flow has varied over the tower histories as it has depended on the availability and capability of its injection system, but attempts are made to keep it as constant as possible. An excessive blowdown rate can triple normal cooling tower treatment costs while inadequate blowdown will quickly escalate the concentration of all soluble species in the already laden systems. Attempts have been made to

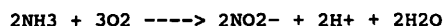
control nitrite/nitrate production rate solely by the blowdown rate but the production rate is too rapid and pH depression will soon occur.

The evaporation rate for the cooling towers is above normal as would be expected in a desert environment. Ambient temperatures can exceed 120 oF in the summer and basin temperature approaches 100 oF. Availability of excess condensate is plentiful in the wintertime but is nonexistent during the hottest days of summer.

ATTEMPTS TO MITIGATE THE AMMONIA OXIDATION REACTIONS

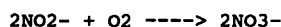
To oxidize ammonia to nitrite requires a large activation energy so it has always been considered likely the route was microbiological and not solely a chemical path. Two alternate paths of nitrite/nitrate production have been proposed and discussed - air-born induction, and an unknown chemical path, perhaps catalyzed by one of the myriad of metals also contained in the tower water. A balance on the nitrogen species and the times of escalation seem to rule out air-born induction, but debate on a chemical reaction path continues.

Conversion of ammonia to nitrite can occur with the following reaction or microbiologically:



The known nitrifying organisms include nitrosomonas, nitrospira, nitrococcus, and nitrosolobus. Their ideal growth rate is an environment between 25 - 30 oC at a pH range of 6 - 8.5.

Conversion of nitrite to nitrate can also be formed through a chemical or biological path:



Known organisms for this conversion are nitrobacter, nitrococcus, and nitrospina, and their ideal growth environment is the same temperature with a slightly narrower pH range between 7 - 8.

Cooling System Fouling

All plant heat exchangers are monitored for efficiency with special attention focused on the surface condenser and on the cooling tower. The surface condensers have experienced some microbiological fouling but biocidal treatment of the inlet water has been effective and inexpensive with the use of halogen chemistry. With proper attention, heat transfer coefficients can be kept at design parameters.

Cooling tower packing fouling has been a major source of concern, however. The desert and plant environments generate ample airborne dust that is scrubbed out of the tower's inlet air, depositing in the packing. In just a few years, the plants accumulated enough solids in their packing to

significantly retard tower performance, necessitating a cleaning attempt. They have removed significant quantities of solids from their packing, regaining efficiency. Since then, however, the tower chemistries have reverted from a nitrate-dominated tower chemistry back to the nitrite-dominated water chemistry seen early in the tower's life. It now appears the biomass appearing in the packing solids transforms the nitrite to nitrate.

DISCUSSION OF GENERAL BIOCIDAL TREATMENTS AND RESULTS

The attempt to retard the production of the nitrite/nitrate ions has emphasized biocides because the main belief among researchers is that the production route is microbiological. Over twenty different commercial biocides have been tried including DBNPA, dodecylguanidine HCl, hydantouin, isothiazolin, quaternary ammonium compounds, and halogens. All have worked to differing degrees on the general microbiological population as measured with plate counts but they have not slowed the conversion of ammonia to nitrite.

Various modes of biocide addition have been experimented with over the years. Shot dosages of various quantities of the plethora of biocides have been applied from the back of the water basin, in the middle, and at the suction of the circulating water pumps. Carbamate was found to be more effective in reducing nitrite when applied from the far side of the tower while controlling surface condenser fouling is best done by applying the biocide near the circulation pumps. Biodispersants have been employed to expose more biomass to the treatment chemicals but they have not had much measurable impact.

DISCUSSION AND RESULTS OF CARBAMATE TREATMENT

There is no doubt the carbamate biocide is the reluctant hero in this tale. It had been discussed early when reviewing the list of potential biocidal treatments but it had always placed low in lab kill rate screenings so it was two years after it was first discussed that it was introduced to the basin as a trial biocide treatment. Overnight, it became the magic bullet. Nitrite production not only stopped, the levels of concentration dropped quicker than the blowdown rate could account for and soon, the nitrite disappeared completely. Initially, nitrite remained absent and the tower pH held over 7.5. After two weeks, the nitrite levels would reappear in their familiar fashion, first one, then two parts per million, then escalating dramatically. The tower was again hit with the carbamate and the nitrite disappeared.

This treatment cycle worked well, but the period between dosages gradually began to shrink, first to ten days, then a week. Eventually, the towers required almost daily doses of carbamate to

control nitrite levels and pH, with costs becoming excessive.

Unfortunately, not much is known about the interaction of the carbamate biocide with the cooling water. Research is currently underway to determine what exactly it does in the tower water. Perhaps a substitute chemical at lower cost could perform a more effective function than carbamate if carbamate mechanisms were better understood.

Most likely, the carbamate doesn't kill the nitrifying population but instead reduces the nitrite and nitrate ions to either nitrogen or ammonia which is then gassed off. Carbamate complexing with the dissolved metal ions has been investigated and as has its by-products.

Two different carbamate molecules have been present due to the different carbamate biocide products marketed by the different water treatment companies and there appears to be a difference in their effectiveness. One product containing both sodium dimethyldithiocarbamate and disodium ethylenebis dithiocarbamate appears to be more effective than another product containing solely the dimethyl carbamate.

With all its weaknesses, carbamate biocide has still been the only proven biocide to retard nitrite production in the tower waters out of more than twenty tested, and it continues to be widely used to reduce nitrite levels, even as it loses its effectiveness.

The regular dosages of carbamate have not proved to be an effective method of controlling general microbiological growth. With regular and exclusive carbamate treatment, the surface condenser tubes still experienced severe enough microbiological fouling to retard heat transfer performance. Another biocide treatment was required to effectively solve this.

DISCUSSION AND RESULTS OF HALOGEN TREATMENT

The biocidal characteristics of the halogens, namely chlorine and bromine, have been employed regularly in liquid form as a treatment to the basin water but have not slowed nitrite formation. The persistent levels of ammonia exclude the sole use of chlorine in the form of sodium hypochlorite (NaOCl) because it will immediately form chloramines which are known to be an ineffective biocide, so it is used in conjunction with sodium bromide (NaBr), forming sodium hypobromite (NaOBr). Bromoamines are thus formed which are a more effective biocide than the chloroamines. While various dosages over various periods have kept the heat exchangers clean, and kept general sessile plate counts to a minimum, nitrite production runs unabated, but halogen chemistry appears to control nitrate production.

The sodium hypobromite and sodium hypochlorite solutions have been applied to the back of the water basin, at the suction and discharge piping of the circulation pumps, at the inlet to the surface condenser, and to the return water header

back to the basin. Via hoses and the wet down systems, it has also been directly applied to the packing and demister pads. Certainly, the surface condenser has been kept clean and efficient with the addition of halogen close to the inlet, but controlling biomass in the basin and packing has been found to be more difficult. This is basically due to the high demand the presence of ammonia incurs and the significant quantities of crickets, beetles, and other insects contributed by the proximity of agriculture. Local, concentrated addition of halogen will not form chloro or bromoamines but has been seen to immediately oxidize ammonia to nitrate generating gas and a local pH of less than 4. Addition of halogen in a diluted form over a wide area has proven more efficient as it maximizes chloro/bromoamine formation without the local oxidation of ammonia and associated pH depression.

The use of gaseous chlorine gas or the generation of chlorine dioxide has been discussed, but not tried due to handling concerns.

CONCLUSION

To summarize, the conversion of ammonia to nitrite is inadequately understood and expensive to control at Magma's four Imperial Valley plants. The only method known so far is the addition of carbamate but the action is not well understood and it is losing its effectiveness. No other biocides have been able to control the production while research continues.

ACKNOWLEDGEMENTS

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