8-1991

The constructed wetlands treatment and reuse of cooling tower blowdown water at General Motor's Saturn plant

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Recommended Citation

Barnett, Mark Oldham, "The constructed wetlands treatment and reuse of cooling tower blowdown water at General Motor's Saturn plant. " Master's Thesis, University of Tennessee, 1991.
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To the Graduate Council:

I am submitting herewith a thesis written by Mark Oldham Barnett entitled "The constructed wetlands treatment and reuse of cooling tower blowdown water at General Motor's Saturn plant." I have examined the final electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Environmental Engineering.

R. Bruce Robinson, Major Professor

We have read this thesis and recommend its acceptance:

Bruce Tschantz, Terry Miller

Accepted for the Council:
Carolyn R. Hodges

Vice Provost and Dean of the Graduate School

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To the Graduate Council:

I am submitting herewith a thesis written by Mark Oldham Barnett entitled "The Constructed Wetlands Treatment and Reuse of Cooling Tower Blowdown Water at General Motor's Saturn Plant." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Environmental Engineering.

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We have read this thesis and
recommend its acceptance:

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Terry L Miller

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The Constructed Wetlands Treatment and Reuse of Cooling Tower Blowdown Water at General Motor's Saturn Plant

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Mark Oldham Barnett
August 1991

DEDICATION

I would like to dedicate this thesis to my parents, Robert and Barbara Barnett. All I can say is thanks.

ACKNOWLEDGMENTS

I wish to thank Dr. R. Bruce Robinson for his guidance and advice. I also wish to thank Dr. Bruce Tschantz and Dr. Terry Miller for serving on my thesis committee. I would like to thank Dr. Bill Miller, Manager Environmental Affairs for the Saturn Corporation for his suggestions and the support of this work. I also wish to thank my friends Brian Benham and Sean O'Neill for the encouragement and most of all, the humor. I am most indebted to my entire family. I would not have gone far without you.

ABSTRACT

General Motor's Saturn Plant in Spring Hill, Tennessee began production in 1990. The Saturn Plant produces up to 736,000 gallons per day of air conditioning cooling tower blowdown water which is currently discharged to the sewer system. This investigation performed a theoretical analysis of the alternative management method of treatment of the blowdown water in a constructed wetlands followed by spray irrigation of crops farmed on site by Saturn. The environmental fate and effect of the inorganic pollutants in the blowdown water was determined by comparison of projected water quality with standards promulgated for wastewater irrigation. For the inorganic pollutants in excess of wastewater irrigation water quality standards, the expected degree of treatment in a constructed wetlands was calculated from precipitation and complexation equilibria. The potential for deleterious metal buildup in the crop soils was also calculated. The fate of the organic pollutants in the blowdown water was determined by review of available information and from a correlation with the octanol/water partition coefficient, a predictor of environmental fate. The suitability of site stormwater runoff for use in the system was also assessed.

The investigation concluded that treatment in a constructed wetlands followed by spray irrigation of crops after supplementation with site stormwater runoff is a potentially attractive alternative to managing the blowdown water. The advantages of such a management alternative include reduction of wastewater disposal costs, conservation of water and sewer capacity, improved crop production and demonstrated public relations. The use of site stormwater runoff would also minimize the plant's impact on the environment

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INTRODUCTION

Background

General Motor's new Saturn plant in Spring Hill, Tennessee began production in 1990. The Saturn plant consists of approximately 2500 acres. Included are separate complexes for powertrain assembly, general assembly, body fabrication and painting, administrative offices and and a central utilities complex. Support areas include streets, parking lots, loading docks and a railroad line. Approximately 300 acres of the site is farmed commercially by Saturn.

The cooling tower at the Central Utilities Complex (CUC) will produce up to 736,000 gallons per day of blowdown water. The blowdown makeup water supply is the public drinking water which becomes more concentrated in the components present in the water supply by repeated cycles of evaporation in the tower. Addition of an organic corrosion inhibitor and biocide also influence blowdown water quality. The blowdown water is currently discharged to the Columbia Publicly Owned Treatment Works (POTW) resulting in approximately $100,000 per year wastewater disposal costs and utilization of available sewer capacity. The Saturn plant will also yield significant quantities of stormwater runoff of unknown quality.

A proposed alternative for managing the blowdown water is treatment in a constructed wetlands followed by spray irrigation of crops. The advantages of this alternative includes the following: reduction of wastewater disposal costs, conservation of water and sewer capacity, improved crop production and demonstrated public relations. The stormwater runoff could also be utilized for crop irrigation or could be treated in the constructed wetlands and discharged, thereby minimizing plant impact on the environment since industrial and urban stormwater runoff can have deleterious effects (EPA, 1983). An important consideration in implementing such a system is assessing the fate of the pollutants in the constructed wetlands, crop soils and the environment.

Spray irrigation with wastewater, primarily municipal wastewater, has been practiced in several arid regions (Pettygrove, 1985). Such systems have successfully conserved water while producing crops satisfactory for human consumption. Careful monitoring is essential to detect and mitigate the introduction of pathogens, carcinogens or heavy metals in deleterious levels into the food chain. Monitoring is also required to prevent the excessive accumulation of heavy metals in the soil.

Constructed wetlands are water inundated areas with aquatic plant growth which are designed and built for treating wastewater or stormwater runoff. Constructed wetlands were conceived after observing the water purifying potential of natural wetlands. Constructed wetlands maximize pollutant removal mechanisms of importance in treating a given wastewater, and avoid the potential ecological consequences of discharging to a natural wetlands.

Constructed wetlands have found increasing use in the United States within the past decade, primarily for the treatment of municipal wastewaters and mine drainage, though other uses, such as for treatment of industrial wastewater, have been more limited (Wieder, et al., 1989). Constructed wetlands have been designed primarily by trial and error or by empirical rules of thumb, so theoretical design basis are scarce. A combination of industrial wastewater treatment followed by spray irrigation of crops is not known to have been attempted previously, so the implementation of such a system by Saturn would be a pioneering technology.

Objective of Investigation

The principle objective of this investigation is to assess the potential for using constructed wetlands followed by spray irrigation of crops to successfully and safely treat the blowdown water. To this end, the specific objectives of this investigation include the following:

1. Identify relevant criteria for acceptable pollutant concentrations in wastewater used for spray irrigation and by comparison with projected blowdown water quality, identify the pollutants of concern which will require treatment in the constructed wetlands and/or dilution with stormwater make-up.

2. Calculate the potential for deleterious metal buildup in the crop soils.

3. For the inorganic pollutants with concentrations in excess of acceptable levels for spray irrigation, the estimated degree of treatment in a constructed wetlands will be determined from precipitation and complexation equilibrium modeling. In particular, metal removal in a constructed wetlands occurs primarily by adsorption/ion exchange and precipitation. Metal removal by adsorption/ion exchange will probably be finite due to exhaustion of exchange sites (EPA, 1988). Mathematical modeling to relate metal concentrations to precipitation and complexation equilibrium in a constructed wetlands would indicate the expected level of long-term metal removal, and would be the first known attempt to mathematically describe metal behavior in a constructed wetlands. The predicted results from the modeling will be compared to the results from an operating constructed wetlands.

For the organic components contributed by the corrosion inhibitor and biocide, the fate and effect in the system will be assessed by review of relevant published information and information provided by the manufacturer. The degree of treatment expected in the constructed wetlands and crop soils will be estimated, where possible, from a correlation with a measured or estimated value of the chemical's octanol/water partition coefficient, a predictor of environmental fate.

4. Perform a conceptual design and cost estimate for the constructed wetlands.

5. Assess the quality of stormwater by comparison with the Nationwide Urban Runoff Program (NURP) results and select the best use of stormwater in the system.

The approach in this investigation is theoretical in nature. Prior to implementation of a constructed wetland crop and wastewater irrigation system for treating the blowdown water, pilot scale or laboratory scale studies are recommended. After implementation of the system, a thorough monitoring and compliance program will be required. However, a theoretical investigation is necessary to assess the potential for using constructed wetlands followed by spray irrigation of crops to successfully and safely treat the blowdown water, to identify the unknown elements requiring further investigation, to identify the key parameters of the system, and to economically justify further investigation.

Chapter 2

LITERATURE REVIEW

Constructed Wetlands

Interest in using constructed wetlands to treat wastewater has increased rapidly during the last decade. This interest was originally spawned by observing the treatment ability of natural wetlands, from intentional or unintentional releases, and many locations have used natural wetlands for treatment (King County Department of Planning and Community Development, 1980). While effective treatment is achievable in many instances, the long-term treatability and effect on natural wetlands ecology is unknown, and the use of natural wetlands for wastewater treatment is discouraged, if not prohibited in many locations.

Constructed wetlands are not normally considered waters of the state, thereby circumventing the problem of ecological impact. Constructed wetlands also offer the advantage of maximizing the features thought to be the most important in treating particular pollutants of importance in a given wastewater resulting in increased efficiency.

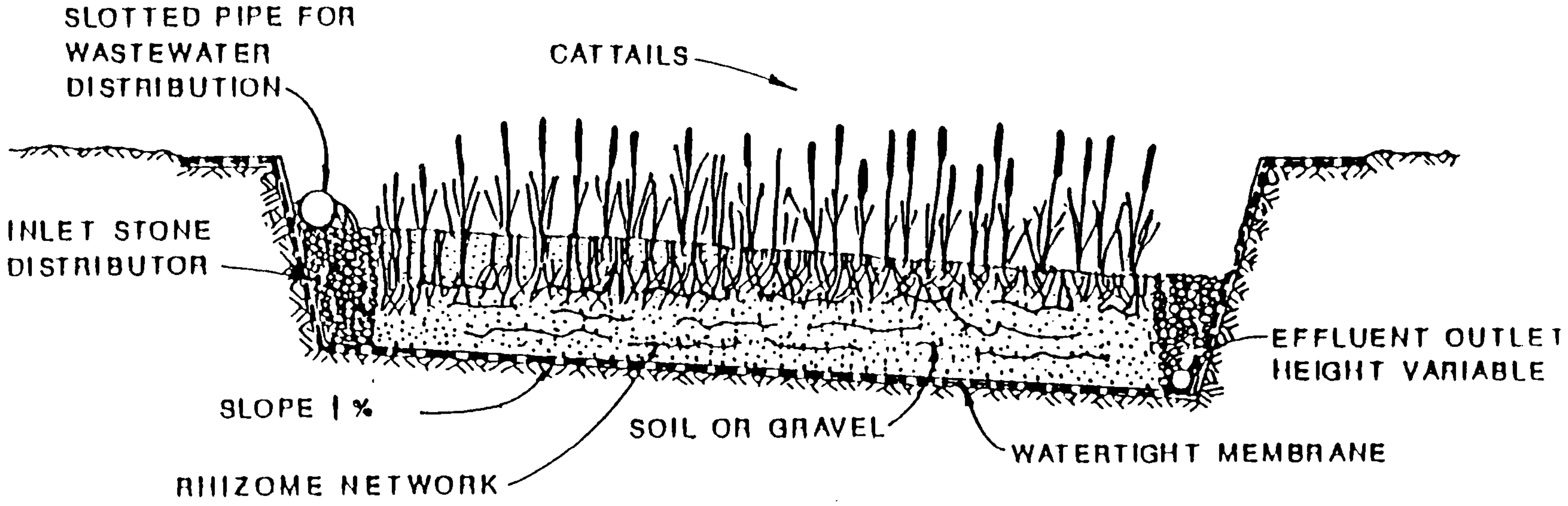
The emergence of constructed wetlands for wastewater treatment has been primarily for municipal wastewaters, with some demonstrations for acid mine drainage and stormwater runoff, but little for industrial or agricultural wastes (Wieder, et al., 1989). However, the use of constructed wetlands for other applications such as minimization of the environmental impact of an urban development (Parkers, et al., 1989) and treatment of landfill leachate (Traufman, 1989) is increasing. Most demonstrations of constructed wetlands have been successful in efficiently removing pollutants from wastewaters. The primary advantage of using constructed wetland is economic, being less capital and energy intensive than conventional wastewater treatment techniques (EPA, 1988). For example, the capital cost of a 1 MGD activated sludge plant with chlorination was $ 1.6 million compared with a constructed wetlands with chlorination capital cost of $0.9 million (Association of Bay Area Governments from Tchobanglous, 1982). Maintenance costs were $ 117,000 per year and $74,000 per year respectively. There are, however, several disadvantages to using constructed wetlands, including land requirements, requiring 4-10 times the land area of conventional wastewater treatment, the potential generation of nuisance odors and organisms, especially mosquitos, and the uncertain continued long-term treatment capacity of constructed wetlands. When properly managed and designed, however, constructed wetlands offer good potential.

Besides the inherit advantage of efficient, economical wastewater treatment, constructed wetlands also provide the added benefits of enhancing wildlife habitat, improving community relations, and adding an aesthetic feature to a plant or community. Amoco's Mandan, North Dakota oil refinery utilizes 1.5 million gallons per day of water from the Missouri River in the production process (Litchfield and Schatz, 1989). Prior to discharge back to the river, the water receives primary treatment by oil-water separation followed by secondary treatment in an aerated bioxidation lagoon. Heavy rains and snows frequently reduced residence times in the lagoon, causing NPDES discharge permit violations. To attempt to eliminate the violations, a 16.6 ha (41 acres) series of cascading ponds were built to provide additional treatment for the lagoon effluent. Cattails, bulrush and other wetland plants naturally invaded the pond system. The bio-oxidation lagoon reduced pollutants by 36 - 99.9% with the cascading ponds serving as a polishing system providing an additional 70 - 100% removal. In 1987, 32 NPDES violations would have occurred for the lagoon alone, including 23 for Total Suspended Solids (TSS) , seven for oil and grease (59.9 kg/day NPDES Standard), one for pH, and one for phenols (1.5 kg/day NPDES Standard). However, the cascading ponds eliminated all of the violations, with an average pollutant removal efficiency of 84% for Biochemical Oxygen Demand (BOD), 70.8% for Chemical Oxygen Demand (COD), 100% for sulfides, 95% for phenols, 95% for oil and grease, 85% for ammonia-nitrogen, 100% for hexavalent chromium, 75% for total chromium and 89% for TSS. The cascading pond system was also significantly cheaper than other conventional wastewater treatment alternatives considered.

Almost immediately, wildlife naturally populated the pond system. To further encourage wildlife migration, 50,000 trees, including 30,000 fruit bearing trees and shrubs, were planted. 184 species of plants now occupy the pond system as do many wildlife species including wood ducks, swallows, Canadian geese, pheasants, partridge, deer, fox, badgers, skunks and raccoons. The ponds were initially stocked with trout, bass and bluegill which have thrived. In the three years since the ponds were constructed, only three NPDES violations have occurred because of high flows due to rain or snow melt. The ponds have also created a pleasing aesthetic attraction for the refinery, and the system has won several national environmental awards.

Types of Constructed Wetlands

Constructed wetlands are generally divided into two categories: free water surface systems (FWS) and subsurface flow systems (SFS) (EPA, 1988). Both systems are basins or channels with shallow, slow-flowing waters and a lined barrier, with either synthetic liner or natural materials such as clay to prevent groundwater contamination. Both systems have emergent aquatic plants, but the FWS has open free standing water, while the SFS consists of below surface water flow with the plants supported in some media, usually sand, soil, or gravel. FWS are initially more economical than SFS because of the bed media costs. SFS can operate at a higher loading rate, however, requiring less land area per unit of flow. SFS also exhibit less problems with odors and mosquitos. Figure 2.1 shows a cross section of a typical SFS.



Source: Environmental Protection Agency Design Manual, Constructed Wetlands and Aquatic Plant Systems for Municipal Wastewater Treatment, EPA/625/1-88/022, 1988.

Figure 2.1 Cross Section of a Typical SFS

Pollutant Removal Mechanisms

The removal mechanisms for the various pollutants are complex, interrelated, and in some cases poorly understood. The plants themselves provide little actual treatment, but support components that maximize treatment capacity (EPA, 1988). For example in SFS, oxygen supplied to microorganisms under the surface via the plant's root system is an important contributor to biochemical oxidation (Watson, et al., 1989).

The primary mechanisms for wastewater treatment are thought to include sedimentation, adsorption/ion exchange, precipitation, decomposition, bacterial metabolism, plant metabolism, and plant adsorption (Watson, et al., 1989). For a given pollutant, one or two removal mechanisms are usually predominant, though many may act in concert to provide treatment. The importance of the adsorption/ion exchange removal mechanism is thought to be the reason SFS, which have larger total surface area (due to the bed media) per unit volume than FWS, can operate more efficiently at higher loading rates for some pollutants, requiring less land area per unit flow .

BOD Removal

Constructed wetlands can be expected to reduce many pollutants, with varying degrees of efficiency, including BOD, TSS, nitrogen, phosphorous, heavy metals, and pathogens (Watson, et al., 1989). BOD removal is accomplished primarily by attached and suspended microbial growth. Microbial organisms may be attached to either plants or media. In FWS reaeration can be accomplished at the water surface, though plant mass or ice can reduce oxygen transfer. Therefore in FWS as well as SFS, oxygen transfer to microorganisms by the plant roots is important. Therefore, for efficient BOD removal, the wetlands depth should not extend below the root penetration depth of the most predominant plants. At the Santee, CA wetlands the root zones of reeds extended 76 cm (2.5 ft), cattails to 30 cm (1 ft), and bulrushes to greater than 60 cm (2 ft) below the surface. Data from 15 sites indicate removal efficiencies increase with organic loadings, and the highest removal efficiencies were for hydraulic loadings less than 7 cm/day (1.72 gal/day/ft2). Total BOD removals ranged from 50-99%.

Suspended Solids Removal

Suspended solids removal can be expected with an efficiency of 50-99% (Watson,et al.,1989). The primary mechanism of suspended solids removal is filtration and settling and often occurs within the first 12-20% of wetland length. Therefore, pretreatment in a sedimentation basin is recommended for wastestreams with high suspended solids concentration to prevent basin blockage from silt accumulations.

Nitrogen Removal

Nitrogen removal is accomplished primarily by nitrification/denitrification with removal efficiencies up to 80% reported (Watson, et al., 1989). Removal by plant uptake is low, typically accounting for less than 10-15% of total nitrogen removal. As with BOD removal, nitrification below the root zone will not occur because of the absence of an oxygen supply mechanism. In FWS, nitrogen removal will be seasonal if anaerobic conditions are produced by ice blockage in the winter or by increased oxygen demand from organic degradation during the summer. Other important factors are minimizing carbonaceous oxygen demand, adequate alkalinity, maintaining pH of 7-8, residence times greater than 5 days, and limiting toxins which can inhibit nitrifiers. Denitrification in the reduced zone of the bottom substrate and litter layer can achieve 95% nitrate removal.

Phosphorous Removal

Phosphorous removals range from 0-90%, and the primary mechanisms are thought to be adsorption, absorption, complexation and precipitation (Watson, et al., 1989). Phosphorous removal in SFS is maximized because of the adsorption removal mechanism. One important consideration is the release of phosphorous after the death of the wetlands plants. Plants absorb phosphorous for transportation to growing tissues. After the plant dies and decomposes, the phosphorous may be partially released. Burial by additional plant litter or sediments may prohibit complete release; however, the potential release of phosphorous by decaying plants demonstrates an interesting phenomenon of constructed wetlands. Constructed wetlands should not be viewed as unlimited sinks or repositories for all pollutants (King County Department of Planning and Community Development, 1980). Wetlands can alter the physical and chemical form of a pollutant and provide storage, and then release them at a different rate. A detention ponds/wetlands system in Orlando, FL demonstrated that decreased detention times and increased turbulence due to storms could release previously removed pollutants (Martin, 1988). However, harvesting of plants, as discussed later, could allow for pollutant removal from the constructed wetlands.

Metal Removal

Metal removal in constructed wetlands occurs by adsorption, ion exchange and precipitation (Watson, et al.,1989). Constructed wetlands have demonstrated an ability to remove a variety of metals with varying degrees of efficiency. Constructed wetlands for controlling non-coal mining operations have been effective in removing lead, zinc, gold, silver and uranium with several possible mechanisms for metal removal noted (Wildeman and Laudin, 1989). For example, metal hydroxide precipitation can occur as bacterial degradation produces bicarbonate and ammonia, raising wetlands pH . Bacteria can also reduce sulfate in the anaerobic zones leading to metal sulfide precipitation. TVA has used several constructed wetlands to control acid-mine drainage from coal mining, and have been effective in removing iron and manganese and raising drainage pH (TVA Office of Natural Resources and Economic Development,1988). To the extent that metals removal is accomplished by adsorption/ion exchange metal removal capacity may be finite due to exhaustion of exchange sites (EPA, 1988). Constructed wetlands in the laboratory have shown finite capacity to remove both nickel (Eger and Lapakko, 1989) and iron (Itenrot, et al., 1989). However, the relative contribution of each mechanism is unknown.

Constructed Wetlands Vegetation

Although under normal conditions in a constructed wetlands, pollutant uptake by the plants is minimal, some aquatic plants can significantly remove pollutants themselves. Conditions for such plant removal, however need to be optimized. Optimum pH, temperature and very long detention times are normally important.

Water hyacinth is a plant noted for its pollutant removal ability. Water hyacinths can be used to either absorb or metabolize and concentrate cadmium, nickel, lead, mercury, copper, chromium, silver, phenols, and carcinogens (Parkash, et al., 1987). In a system with a sixteen day hydraulic detention time, Parkash showed that 82-92% of cadmium was removed by the plants, and cadmium removal from water increased linearly with initial concentrations. Careful study was recommended prior to disposal of hyacinths harvested from the system.

Duckweed is another aquatic plant with renovation potential, and an ability to treat municipal wastewater to an acceptable level for agricultural irrigation (Ora, et al., 1986). Duckweeds were noted to be superior to water hyacinths in that they were more hardy,more resistant in temperate climates, caused less evaporation losses, and could be harvested as animal feed. Removal efficiencies of 50-60% for major pollutants has been reported with the duckweed fronds as well as the roots being able to absorb nutrients. Growth rates for duckweeds are high, on the order 0.1-0.35 gram/gram/day, but duckweeds are easily harvested because they tend to form a dense floating mat at the water surface which may be skimmed from the water with minimal cutting. This dense mat can also reduce evaporation water loss by 20%, which would conserve water. Harvested duckweeds can also offset treatment costs by $0.04 /cubic meter when used for animal fodder. Duckweeds are among the most hardy growing plants and will thrive under varying environmental conditions.

Waterweed is another water plant with pollution renovation potential (Bishop and Eighmy,1989). Waterweeds were found to compare favorably in BOD, nitrogen, and phosphorous removal to water hyacinths, and were much hardier in temperate climates. Also, the production of anaerobic conditions brought about by the dense surface mat caused by duckweeds, was not noted. A control system of aquariam plants and actual waterweed was used to determine the degree of pollutant removal attributable to the biofilm growth on the plants. At detention times of 2.3-4.6 days, BOD removal averaged 89% and nitrogen removal 57% in summer and 18% in winter. The removal was found to occur primarily by the biofilm. Although waterweeds were more productive in general during the summer, they were useful year round.

Although most plants do have some capacity to remove metals by incorporation into plant tissue (i.e. water hyacinths), plant uptake is secondary to physiochemical removal mechanisms (Association of Bay Area Governments,1982). An SFS in Santee, CA received copper and zinc laden wastewaters, and removed the metals with 97-99% efficiency with less than 1% of the total metal removal attributed to plant uptake (Gersberg, et al., 1984) with the remaining removal attributed to precipitation and adsorption/ion exchange. This seems to indicate that although some plants can absorb and concentrate metals, under the normal operating conditions of constructed wetlands metal uptake by the plants is not significant when compared to total metal removal. However, because plant harvesting and disposal may be periodically required, at least initially the metals contents of aquatic plants should be analytically measured.

Constructed Wetlands for Treating Wastewater - Case Studies

Many constructed wetlands across the country have reported removal efficiencies of various pollutants. Most reflect the primary concerns for municipal wastewaters. TSS, BOD, nitrification/denitrification and phosphorous removal efficiencies are well documented. Constructed wetlands used for acid mine drainage have reported results for removal of many metals, though primarily iron and manganese. Other pollutants have little if any information on removal available in the literature. For pollutants with documented removal efficiencies, these are often widely variable between different constructed wetlands, and are often widely variable with time in individual wetlands. Several case studies demonstrate the reported range of removal and benefits of constructed wetlands.

Tennessee Valley Authority

TVA experienced continued, chronic water quality discharge violations from the sedimentation basin of the 950 coal mine in Jackson County, Alabama (Brodie, et al., 1989.a.). The average discharge flows ranged from 0-380 L/min (0-100 gpm) and a constructed wetlands of 0.13 ha (0.32 acres) was used. The wetlands was planted with 16,000 cattails and woolgrass then fertilized and limed. The wetlands has been able to increase pH from 6.1-6.9, reduce iron from 14.3 mg/L to 0.8 mg/L(94% removal), manganese from 4.8 mg/L to 1.1 mg/L (77%) and TSS from 24 mg/L to 7 mg/L(71%). Since operation, the wetlands has eliminated the frequent water quality violations. The cost of the constructed wetlands was also significantly cheaper than the cost of attempting to modify the sedimentation basin. Prior to construction, only two taxa were observed in the creek receiving the discharge from the sedimentation basin. Only 6 months after construction, 19 taxa were collected. Only two taxa were initially planted in the constructed wetlands, and 32 were collected within six months. The only operational problem has been with muskrat damage to the dike which necessitated repair.

Because of the success of the 950 coal mine wetlands and others, TVA added constructed wetlands to treat ash pond seepage at the Widows Creek Steam Plant in Jackson County, Ala., the Kingston Steam Plant in Roane County, TN and the Colbert Steam Plant in Colbert County, Ala.(Brodie, et al., 1989.b). The Widows Creek Plant had 39 ha (96.4 acres) active ash pond storage. In April 1986 a 0.5 ha (1.2 acres) wetlands was constructed with cattails, rush and bulrush in a total of three cells in series. A very heavy infestation of armyworms caused severe defoliation and reduced treatment efficiency during the first two summers. The Widows Creek constructed wetlands reduced an average influent concentration of 186 mg/L of iron by 97%, but only reduced manganese influent concentration of 7.1 mg/L by 7%. The pH decreased by an average of two units in the first eight months, requiring installation of a sodium hydroxide drip feed system to increase effluent pH prior to discharge.

The Kingston plant had 14 ha (35 acres) of active and 91 ha (225 acres) of retired ash pond storage, and a 0.9 ha (2 acres) wetlands was constructed. The average flow to the wetlands had iron concentrations of 170 mg/L which were reduced by 85%. Little if any manganese removal was observed, and the pH decreased by 3 units though the reason was not determined. The wetlands will require additional chemical treatment until performance improves. High length to width ratios were postulated by the authors to have reduced treatment efficiencies, though the rationale for the postulation was not given.

The Colbert Plant wetlands was constructed by enlarging the size of a natural wetlands to 1 ha (2.5 acres). The Colbert wetlands exhibited good pH control but manganese concentrations actually increased initially. The increase was attributed to flooding of the natural wetlands which contained significant amounts of previously deposited manganese.

The Danka Mine

Constructed wetlands have also been used to treat mine drainage from non-coal mines, removing metals other than iron and manganese with varying success (Wildeman and Laudin,1989). LTV Steel Mining Company's Danka Mine in Minnesota, utilized a natural wetland to receive drainage with average concentrations of 18 mg/L nickel and 0.62 mg/L copper. Treatment efficiencies were 84% and 92% respectively with peat uptake accounting for most metal removal. Constructed wetlands have also been used to remove lead, zinc, gold, silver, and uranium. Sulfides, oxides and carbonates were noted to be the most thermodynamically stable metal precipitates, and constructed wetlands should ideally maximize formation of these precipitates rather than organic forms, which could potentially be released. It was also noted that bacterial degradation of organic material in the wetlands will generate ammonia and bicarbonate, raising the pH and enhancing metal precipitation.

Wildwood, Florida

A natural wetlands, in Wildwood, FL received wastewater from a small city and runoff from a 672 ha (1660 acres) watershed for over twenty years (Association of Bay Area Governments, 1982). The wetlands consisted of approximately 200 ha (500 acres), including a swamp populated with duckweed, cattail, and willow followed by two hardwood swamps. The wetlands treated an average of 570 cubic meters/day (150,000 gal/day) of flow, with an average removal of 0% for copper, 85% for iron, a net increase in magnesium, 60% for lead and 75% for zinc . Low metals build up in the marsh was thought to be the result of relatively low metal content of the domestic wastewater effluent.

Brookhaven National Laboratory

A combination marsh/meadow/pond system has been used since 1983 to treat domestic wastewater up to 80 cubic meters/day (21,000 gal/day) from the Brookhaven National Laboratory in Long Island, NY (Association of Bay Area Governments, 1982). The meadows consisted of reed canary grass, and other grasses and weeds. The marsh was filled with mulch and cattails, and an 80 square meter (860 square feet) pond with duckweed was used to stabilize the effluent. Removal efficiencies were 60% for chromium, 94% for copper, 85% for iron, 23% for magnesium, 85% for zinc and 91.5% for suspended solids.

Santee, California

An SFS in Santee, CA conducted a controlled experiment to measure the metals removal in a constructed wetlands (Gersberg, et al., 1984). The constructed wetlands was designed to treat municipal wastewater and wastewater treatment plant effluents. The constructed wetlands received secondary effluent from an activated sludge process, and the flows were artificially enriched with cadmium, copper and zinc with the pH lowered to 5.5. The constructed wetlands reduced copper from 9.26 mg/L to 0.056 mg/L for a removal efficiency of 99% at an application rate of 8 cm/day (2 gal/day/square feet). Another cell also received copper at 10.68 mg/L and produced an effluent of 0.059 mg/L for a removal efficiency of 99% at an application rate of 4.7 cm/day (1.2 gal/day/square feet). Zinc was reduced from 11.28 mg/L to 0.37 mg/L for a removal efficiency of 97% at an application rate of 4.7 cm/day (1.2 gal/day/square feet). Cadmium was reduced by 99% from 0.532 mg/L to 0.004 mg/L at the same application rate. The experiment was conducted from late 1982 to June 1984 and only the zinc amended bed showed a decrease in removal efficiency, but the efficiency never dropped below 88%. A blue substrate was noticed to coat the bed litter and gravel of the copper amended beds, probably indicating the importance of the precipitation removal mechanism. Plant uptake was calculated to account for less than than 1% of the copper and zinc removal. Harvesting of the biomass was also required once or twice per year.

Windsor Coal Company

A constructed wetlands at the Windsor Coal Company in West Virginia was built with limestone, sterile mushroom compost and cattails (Kolbash and Romanoski, 1989). After only one growing season the constructed wetlands was able to reduce iron concentrations by 50%, from the runoff from a 12 ha (30 acre) refuse pile.

A summary of case studies is shown in Table 2.1.

Constructed Wetlands for Treating Stormwater Runoff - Case Studies

Several case studies have also been reported for treating stormwater runoff in a constructed wetlands.

Table 2.1 Summary of Case Studies of Constructed Wetlands for Treating Wastewater

Location	Wastewater	Wetlands Size / Type	Hydraulic Loading (Acres/MGD)	Treatment Efficiency	Removal (lbs/ acre - year)
TVA - Jackson County, Alabama 950 Coal Mine	Acid Mine Drainage	0.32 acre	9.7	Fe 94% Mn 77% TSS 71 %	4240 1162 5339
TVA - Jackson County, Alabama Widows Creek Steamplant	Ash Pond Seepage	1.2 acre (based on original size)	18.6	Fe 97% Mn 7%	29,546 98
TVA - Roane County, Tennessee Kingston Steam Plant	Ash Pond Seepage	2 acre	4.3	Fe 85% Mn 0 %	102,370 0
LTV Steel Mining Company,Minnesota The Danka Mine	Acid Mine Drainage	Natural Wetlands		Ni 84 % Cu 97%	
Windsor Coal Company West Virginia	Mine Refuse Drainage	Limestone, sterile mushroom compost and cattails		Fe 50% (1 growing season)	

Table 2.1 (Continued)

Location	Wastewater	Wetlands Size / Type	Hydraulic Loading (Acres/MGD)	Treatment Efficiency	Removal (lbs/ acre - year)
Wildwood, Florida	Municipal Wastewater	1660 acre Natural Wetlands	3333	Cu 0 %	
				Fe 85 %	
				Pb 60 %	
				Zn 75 %	
Brookhaven National Laboratory Long Island, New York	Domestic Wastewater	Meadow/Marsh/Pond		Cr 60%	
				Cu 94%	
				Fe 88%	
				Mg 23%	
				Zn 85%	
				TSS 91 %	
Santee, California	Metal Enriched Wastewater	SFS	20	Cu 99%	1618
			12	Cu 99%	2336
			20	Zn 97%	1662
				(decreased to 88%)	(decreased to 1512)
			20	Cd 99%	80
Manden, North Dakota Refinery	Industrial Wastewater	Cascading Ponds, Lagoons	59	BOD 84%	1315
				COD 71%	4823
				Sulfides 100%	281
				Phenols 95%	4
				Ammonia 85%	4
				Oil/Grease 95%	400
				Cr(+6) 100%	0.2
				TSS 89%	1853

Freemont, California

In Freemont, CA, a constructed wetlands was built in 1983 to treat stormwater runoff from a 1200 ha (2963 acre) watershed (Meiroin, 1989). The watershed consisted of 66% low-density residential, 28% agricultural/open, 5% high-density residential and 1% roadway and commercial. The wetlands consisted of 22 ha (54 acres) and was divided into 3 separate subsystems including an open water lagoon, overland flow followed by ponds with underwater sills and a channel with heavy cattail and brush operating in combination series and parallel. The entrance to the constructed wetlands consisted of a 0.15 ha (0.37 acre) debris basin which served to distribute flow. The hydraulic capacity of the system was 71,700 cubic meters (19 million gallons) which was sufficient to hold all the runoff from a large storm. Although some short-circuiting was noticed, detention times ranged from 1-14 days.

Each subsystem showed different removal potential for each pollutant, with the ponds and lagoons generally reducing the bulk of the suspended solids removal. In the overland flow subsystem, metal loadings in the effluent sometimes exceeded influent concentrations due to resuspension of particulate matter during high turbulence events. The overall system was able to removal pollutants with 64% efficiency for TSS, 68% for chromium, 31% for copper, 88% for lead, -111% for manganese, 20% for nickel and 33% for zinc. Saline groundwater infiltrating the wetlands caused an overall 99% increase in TDS.

Wayzata, Minnesota

A natural peat wetland in Wayzata, Minnesota was used to treat stormwater runoff from a 26.3 ha (65 acres) watershed. (Association of Bay Area Governments, 1982). The wetland itself was 3.1 ha (7.7 acres), and the watershed consisted of a mixture of urban area and open wooded areas. The wetlands exhibited removals of 94% for suspended solids, 25-80% for cadmium, 13-83% for copper, 90-97% for lead and 78-86% for zinc. A water balance on the wetlands indicated inflows were 35% precipitation, 47% from the runoff of the watershed, and 18% from groundwater. Effluent water losses were 25% evapotranspiration and 75% surface discharge.

Montgomery County, Maryland

A stormwater detention pond for a 60 ha (150 acres) watershed in Montgomery County, Maryland treats runoff from shopping malls, roadways, and apartment complexes (Association of Bay Area Government, 1982). The 2.4 ha (6 acres) pond is lined with wetlands vegetation. Removal efficiencies indicate 98% removal for cadmium, 96% for iron, 96% for lead and 99% for zinc. The Montgomery pond indicates an interesting phenomenon in treating stormwater runoff. Large permanent ponds or lakes with diverse biological activity can serve as both peak flow reducer, i.e. flow equalizer, for runoff as well as an efficient removal system for stormwater pollutants.

Lake Ellyn, Illinois

Lake Ellyn, a 4.1 ha (10.1 acre) lake in the Chicago Metropolitan area receives runoff from a 21,350 ha (53,374 acre) area, including 83% residential, 5% commercial, 7% open area, and 5% urban (Striegl, 1987). The lake is very efficient in removing suspended materials, with removal efficiencies of 76-94% for copper, iron, lead and zinc. The lake also removed to a lesser extent arsenic, cadmium, chromium and mercury. Metals, however, were observed to concentrate in lake sediments and even metals present in low concentration in the runoff were observed to concentrate, which would cause an eventual buildup of metals in the lake.

Orlando, Florida

A detention ponds-wetlands system in Orlando, Fla was used to treat runoff from 16.8 ha (41.6 acres) consisting of land uses of 33% urban roadway, 28% forest and 40% residential. (Martin, 1988). The pond was lined with cattails and had depths ranging from 8 ft during dry weather to 11 ft in wet weather. The wetlands itself consisted of cypress trees, water hyacinths, duckweeds, and cattails over 0.30 ha (0.73 acres). Wetlands depths ranged from 0-3 ft during dry weather to 5 ft during storms. The detention pond was effective in reducing suspended solids, lead and zinc primarily by sedimentation. Increased turbulence and decreased detention times during storms caused pollutants to be washed from the detention pond. However, heavy vegetation could reduce wash out of suspended pollutants.

Table 2.2 provides a summary of the case studies for wetlands treatment of stormwater runoff.

As evidenced by the case studies, pollutant removals from wetland to wetland are often varied. Variances in wetlands and vegetation types, loading rates and temperature make exact prediction of wetlands removal efficiencies difficult (Lakatos, et al., 1987). Other pollutant removal complexities observed included interaction with groundwater and biological productivity (USGS, 1986).

Design Equations

Because of the complexity and uncertainty of pollutant removal mechanisms in constructed wetlands, theoretical design bases are not generally available. However, design equations based on BOD removal and first order, plug flow kinetics have been proposed (Reed, et al., 1988). For first order BOD removal kinetics, the basic design equation is given by

$$\frac{C_e}{C_o} = \exp(-Kt) \qquad (2\text{-}1)$$

where C_e = Effluent BOD_5 (mg/l),

C_o = Influent BOD_5 (mg/l),

K = Temperature dependent, first order rate constant, days^{-1}

t = Hydraulic residence time, days.

Table 2.2 Summary of Case Studies for Wetlands Treating Stormwater Runoff

Location	Watershed	Wetlands Size / Type	Removal / Treatment
Freemont, California	2963 acre watershed	Overland Flow, Ponds and Channels	TSS 64% Cr 68% Cu 31% Pb 88% Mn -111% Ni 20% Zn 33%
Wayzata, Minnesota	65 acre Mixed Urban/Open Watershed	7.7 acre Natural Peatland	TSS 94% Cd 25-80% Cu 13-83% Pb 90-97% Zn 78-86%
Montgomery County, Maryland	150 acre Urban/Open Watershed	6.2 acre Pond with Wetlands Vegetation	Cd 98% Fe 96% Pb 96% Zn 99%
Lake Ellyn, Chicago	53,374 acre Urban/Open Watershed	10.1 acre Lake	Cu 76-94% Pb 76-94% Zn 76-94% Fe 76-94%

The first order reaction rate constant can be corrected for temperature by (Reed, et al., 1988)

$$K = K_{20}(1.1)^{T-20} \qquad (2\text{-}2)$$

where K = Reaction rate constant at Temperature = T °C

K_{20} = Reaction rate constant at 20 °C

The hydraulic residence time is given by

$$t = \frac{L\,W\,d\,n}{Q} \qquad (2\text{-}3)$$

where L = Wetlands length, m

W = Wetlands width, m

d = Wetlands depth, m

Q = Wastewater flow rate, cubic meters/day

n = Porosity of system (as a fraction)

The value of porosity is the fraction of the wetlands volume not occupied by other substances and available for water flow. For an FWS, n is controlled by the density of plant growth, while for an SWS, n is controlled by the porosity of the bed media.

The basic design equation for FWS has been proposed from experience with overland flow and trickling filters (Reed, et al., 1988) as

$$\frac{C_e}{C_0} = A \exp \frac{-0.7\,K\,(A_v)^{1.75}\,L\,W\,d\,n}{Q} \qquad (2\text{-}4)$$

where A = Fraction of BOD_5 not removed as settleable solids

A_v = Specific surface area for microbial growth, m^2/m^3

The recommended coefficients for FWS are (Reed, et al., 1988)

$A = 0.52$

$K_{20} = 0.0057\ d^{-1}$

$A_v = 15.7\ m^2/m^3$

$n = 0.75$

For SFS equations 2- 1 to 2-3 can be combined to provide the design equation

$$\frac{C_e}{C_o} = \exp \frac{-K\,L\,W\,d\,n}{Q} \qquad (2\text{-}5)$$

The required cross sectional area of an SFS, width times depth, is also given by Darcy's equation

$$Q = k_s W d S \qquad (2\text{-}6)$$

where k_s = hydraulic conductivity, $m^3/m^2/day$

S = Slope of the bed

For an SFS typical values of K_{20} are 1.28 d^{-1} and S = .01 (EPA, 1988).

Because design equations for pollutants other than BOD have not been proposed, and BOD removal is often influenced by many factors other than those postulated by the design equations, most constructed wetlands are designed based on empirical rules of thumb for loading rates, etc. Because of these uncertainties, design of a constructed wetlands based only on the kinetic equations is not recommended (EPA,1988).

Hydraulic Loading Rates

As with removal efficiencies, hydraulic loading rates for constructed wetlands reported in the literature also vary widely. The EPA has reported hydraulic loading rates in the range of 23.4-37.4 acres/MGD as typical (EPA,1988). The 1986 Symposium on surface mining proposed a rule of thumb of 3.2 acres/MGD (Weider,1989). Watson, et al. (1989) summarized rates reported in the literature for municipal wastewaters and acid mine drainage. Tchobanoglous and Culp reported municipal systems had hydraulic loading rates of 1.5-112 acres/ MGD. A Bureau of Mines Survey reported average values of 10.2 acres/ MGD.

TVA summarized experience based on 11 constructed wetlands for treating acid mine drainage (Brodie, et al., 1988). In general, the TVA wetlands for acid mine drainage were sized to treat the flow from a 10 yr, 24 hr storm and then increased if water quality was not as expected. The resulting hydraulic loading rates were 2.3-72 acres/MGD for average flow and 1.3-26.7 acres/MGD for peak flow.

The SFS in Santee, CA which demonstrated removal of cadmium, zinc and copper under controlled conditions is probably best representative of hydraulic loading rates applicable to Saturn. The hydraulic loading rates ranged from 12-20 acres/MGD with high metals removal efficiency (Gersberg,et al., 1984). Higher hydraulic loading rates were considered possible.

The wide range of hydraulic loading rates presumably reflects the inadequate design basis to date of constructed wetlands. Table 2.3 summarizes the values reported for hydraulic loading rates.

Configuration

Length to width ratios (L/W) are another key design parameter. L/W ratios of >10/1 are recommended for FWS to ensure plug flow conditions and to minimize short circuiting (Watson and Hobson, 1989). However, for SFS, L/W ratios of <3/1 and typically 1/1 are recommended to ensure flow remains subsurface. Depths, as noted earlier are normally determined by root penetration to meet oxygen demands. Slopes for typical SFS are 0-1% and failure to include Darcy's law (Equation 2-6) in SFS design has resulted in above surface flooding in some SFS.

Flow patterns, wetlands layout, and feed locations are all key parameters in wetlands design (Steiner and Freeman, 1989). Flow patterns available include plug flow, step feed and recirculation. Single wetlands cells are the simplest and least expensive, but provide no redundancy for maintenance and are therefore only recommended for low flows. Parallel cells allow continued treatment during maintenance on other cells (although at lower overall efficiency). Besides routine maintenance requirements, mosquito control is enhanced by periodic draining. Wetlands cells in series can utilize different wetlands types (for example, a FWS cell followed by a SFS cell) to achieve optimal treatment by providing a greater variety of removal mechanisms. Series cells, however, lack maintenance flexibility unless independent wastewater distribution to each cell is provided. Recirculation of flow can enhance biological treatment by decreasing inlet

Table 2.3 Typical Wetlands Size

Source	Recommended or Reported Loading Rates (Acres/MGD)
EPA Design Manual	23.4 - 37.4
Bureau of Mines, 1983	10
Pasavento/Weider, 1983	3.2
TVA, 1988	1.3 - 26.7
Watson, et al., 1989	1 - 40
Gersberg, 1984	12 - 20

pollutant concentrations (and the associated potential for odors) and increasing oxygen concentrations.

Costs

The costs for constructed wetlands are also varied, and a summary of the range of reported costs for constructed wetlands is shown in Table 2.4. Typically SFS are more expensive than FWS because of the initial bed media costs, as noted earlier. Two FWS for treating municipal wastewater in California, Arcata and Gustine, were constructed at a cost of $16,600 per acre and $38,000 per acre respectively (EPA, 1988). A Bureau of Mines survey found that wetlands were constructed at an average cost of $12,000 per acre (Weider, et al., 1989). TVA has constructed a total of eleven wetlands varying in costs from $14,500 per acre to $130,000 per acre with an average cost of $49,000 per acre (Brodie, et al., 1988). Although great variation in cost per acre was noted, $40,000 per wetlands was thought to be representative. TVA broke down the construction costs into an average of 20% for design and project management, 35% for equipment and supplies, and 45% for labor with an annual maintenance cost of only $1,000 per wetlands per year.

Saturn performed a detailed cost estimate resulting in a projected cost of $139,000 per acre.

Corrosion Inhibitor and Biocide

The blowdown water from the Saturn plant will contain several organic compounds form the addition of a corrosion inhibitor and biocide. The corrosion inhibitor will contribute tolytriazole, two phosphonates (HEDP and PBTC) and an acrylic acid polymer. The biocide will contribute two isothiazolin biocides. The specific identity of the organic compounds and the expected concentrations are discussed in Chapter 4. In conducting the literature review for the

Table 2.4 Typical Wetlands Construction Cost

Source or Location	Costs (Dollars per Acre)
Arcata, California	16,600
Guistine, California	38,000
Bureau of Mines Survey	12,000
TVA	14,500 - 130,000
Saturn (Detailed esimate performed by Saturn)	139,000

environmental fate and effect of the organic chemicals contributed by the corrosion inhibitor and biocide, the following methodology was used. The Chemical Abstracts Date Base and Syracuse Research Corporation's Environmental Fate Data Base were used to identify relevant publications. Dexter Chemical, Saturn's supplier provided relevant information and supplied Material Safety Data Sheets and some toxicity information (Tschantz, et al., 1990). A discussion of the published material used in assessing the chemical's behavior in the system considered is included below. The conclusions of this assessment are presented in Chapter 4.

Steber and Wierich (1986) studied the biodegradability, adsorption and mobility in soils, and the potential for bioconcentration of phosphonic acid, (1-hydroxyetylidene)bis-(HEDP), one of the components of the corrosion inhibitor present in the blowdown water at a predicted concentration of 1.7 mg/l. Previously, Huber had demonstrated that HEDP did not biodegrade, but noted that the acute aquatic toxicity of HEDP was low. This result was confirmed; After 30 days the biochemical oxygen demand (BOD) was measured as less than 10% of the chemical oxygen demand (COD). Degradation in soils was found to be dependent on soil type, but was still very low, degrading only by 5% after two months. Anaerobic degradation was measured in an anaerobic sludge digester, and was again very low, degrading by less than 5% even after 20 weeks in the digester.

However, photodegradation to acetate was found to take place. Degradation in a light environment increased by 4 to 20 times over incubation in a dark environment, and the addition of photoxidation inhibitors significantly decreased degradation. Light in the spectrum of sunlight particularly enhanced degradation, and degradation was seen to decrease with increasing water depths, and slowly approached dark values.

Adsorption of HEDP on different sludges from sewage treatment plants was significant, adsorbing >90% of applied HEDP after 24 hours. The adsorption onto soils occurred to a lesser extent, but was still significant. Adsorption was dependent on soil type, and the linear Fruendlich isotherm constant, K, measured for several different soil types ranged from 20 - 190 which was compared to the EPA classification system of 10 < K < 100 for compounds moderately mobile in soils and 100 < K < 1000 for compounds slightly mobile in soils. The soil adsorption constant (ratio of amount of HEDP adsorbed to the amount initially present) from the same soils varied from 0.80 - 0.96. Bioaccumulation was measured with zebra fish in HEDP amended waters. The bioconcentration factor (BCF), the ratio of the concentration in fish to the concentration in water at equilibrium, was measured at 20. Compounds with BCF < 50 were noted to have low bioconcentration potential.

The study concluded that although biodegradation did not occur, HEDP should not be environmentally persistent because of photodegradation. HEDP was found to be moderately to slightly mobile in soils, with low leaching potential. HEDP was concluded to have very low potential for bioaccumulation.

Horstmann and Grohmann (1988) studied the biodegradability of six phosphonates, including HEDP and 1,2,4 butanetricarboxylic acid, 2-phosphono (PBTC), another component of the corrosion inhibitor present in the blowdown water at a predicted concentration of 1.6 mg/l. Neither of the compounds was found to biodegrade, though HEDP was thought to be more biodegradable than PBTC. However, significant adsorption on sewage treatment sludge was noticed, reducing the phosphonates by 50 - 80% within the first few days. For HEDP, this result was consistent with the work of Steber and Wierich. The conclusion of the study was that biodegradation of neither of these compounds was likely in the environment, and therefore, the use of these compounds should be discouraged.

Syracuse Research Corporation (1977) reviewed the literature on the environmental fate and effect of benzotriazoles, a class of organic compounds. Tolytriazole (a methyl benzotriazole), one of the components of the corrosion inhibitor present in the blowdown water at a predicted concentration of 1.6 mg/l, was included in the study. Benzotriazoles as a group of chemicals have the potential to be environmentally persistent, not oxidizing or hydrolyzing in the environment. Evidence of photodegradation is not clear, but the compounds will probably be stable under sunlight irradiation. Certain members of the benzotriazole family are used as light stabilizers in plastics.

Calculations suggest that tolytriazole will not bioaccumulate appreciably in food chain organisms. Occupational and epidemiological studies had not been conducted, but no poisonings were reported. The manufacturer reported that benzotriazoles were very low toxicity and low health hazard chemicals. However, tolytriazole was cumulatively toxic (lethal concentrations decreased with longer exposure times) to fathead minnows, having a 96 hour LC_{50} of 25.5 mg/l. The 96 hour LC_1 was 14.2 mg/l. In an effort to judge the effect of tolytriazole on wastewater treatment plant microorganisms, microorgaism population was measured over time with exposure to tolytriazole. Although the evidence for biodegradation was not clear, concentrations of tolytriazole less than 20 mg/l were not significantly toxic to microorganisms. However, higher concentrations may be toxic to microorganisms. The LD_{50} for oral administration in rats for tolytriazole was reported as 675 mg/kg. Exposure to benzotriazole dusts was thought to be extremely hazardous. Several benzotriazoles (tolytriazole was not tested) were also shown to exhibit teratogenetic effects on frog embryos. Benzotriazole was being investigated as a potential carcinogen at the time of publication and the results were not reported. However, tolytriazole and the other organics in the corrosion inhibitor and biocide have not been investigated as potential carcinogens (US Department of Health and Human Services, 1989).

Benzotriazoles could also adversely effect plants. The effect of tolytriazole was not determined. Application of 50 mg/l of benzotriazole to tomato plant roots caused deleterious effects, including reduced formation of leaflets. However, applications as high as 1,000 mg/l to plant foliage had no adverse effect. Applications of 133 mg/l of benzotriazole caused 50% root repression in cucumbers. Applications of 1,330 mg/l of benzotriazole to the soil of bush bean plants caused morphological changes.

Krzeminski, et al., (1975a) studied the environmental fate and effect of 5-chloro-2-methyl-4-isothiazoline-3-one and 2-methyl-4-isothiazoline-3-one, two microbiocides present in the biocide at shock concentrations. Biodegradation did occur, although significant lag times were noted while the microorganisms acclimated to the compounds, requiring 2 - 3 weeks of acclimation before degradation of a 1 mg/l solution of the chlorinated isothiazoline-3. The chlorinated isothiazoline-3 degraded at a slower rate because of a higher microbicidal activity, degrading by 90% in 5 days in river water with an acclimated seed. Complete degradation to carbon dioxide was slower, with 50% degradation in approximately 40 days. Photodegradation occurred at a much faster rate, with 48% and 61% reduction of the two compounds respectively after 48 hours. Adsorption studies with river silt showed neither compound will adsorb effectively, adsorbing less than 11% after 20 hours contact with river silt. Both compounds were rapidly absorbed and metabolized by the aquatic plants duckweed and salvinia. In a test with salvinia uptake of ^{14}C labeled chlorinated isothiazoline-3, 60% of the ^{14}C activity was extractable in methanol after 1 day and 30% of the ^{14}C activity was extractable after 3 days. No detectable concentration of the parent compound was detected in either extraction, indicating rapid metabolism to carbon dioxide, which was confirmed in a later experiment. Soil biodegradation occurred more completely and at a higher rate than did aqueous degradation, which was attributed to the greater diversity of biological activity in the soil. The two compounds were found to bioconcentrate slightly, with BCF measured from 6 - 310, which was reversible upon return to non-contaminated water, reducing fish levels by 50% in less than a week. Rats were found to eliminate both compounds via excretion with a biological half-life of less than 1 day. Tissue storage of the compounds in rats was less than 2.1%. The study concluded that in low levels found in most applications of 0.01 mg/l - 1 mg/l, the tissue storage capacity of these compounds is minimal in rats and fish , and that multiple degradation pathways would eliminate the compounds rapidly as discussed above, causing no adverse effect to the environment.

Krzeminski et al., (1975b) also studied the degradation products of the two isothiazolines. The first primary degradation product is N-methlymelanomic acid which is approximately 50 times less toxic than the two compounds. The two compounds were found to degrade rapidly by chemical, biological and photoxidative means to less harmful intermediates. A 0.1 mg/l concentration of the chlorinated 3-isothiazoline was found to degrade by 75% in four days in river water, with 83% conversion to carbon dioxide after 22 days. Biological degradation was thought to be the most important degradation pathway in the environment, because photodegradation would only occur in shallow waters. Chemical degradation was not thought to be important at the pH of most natural waters. Biochemical degradation would also be expected to occur more rapidly for microorganisms acclimated to the biocides, a condition which would be met in a constructed wetlands receiving blowdown effluent containing these two biocides. The results of this study concluded that discharge of the biocide should not adversely impact aquatic ecology.

Scribner, et al. (1983) reported results of toxicological investigations of a biocide containing the 3-isothiazoline compounds. The biocide was not thought to exhibit carcinogenic or mutagenic tendencies, under normal applications in the range of 1 - 25 ppm.

Uptake of several biocides, insecticides and herbicides have been summarized for several constructed wetlands and aquatic treatment systems (Association of Bay Area Governments, 1982). Although many plants have an ability to absorb and metabolize biocides, other plants can concentrate biocides in plant tissues, where consumption of these plants could cause deleterious effects for the consumer. Because plants vary in their uptake and concentration potential for different biocides, analytically measuring the concentration in plants prior to disposal is warranted.

Dexter Chemical, Saturn's supplier provided some product information which is helpful in judging environmental fate and effect (Tschantz, et al., 1990). From the product information, PBTC is essentially non-toxic by digestion, but may cause slight irritation to the eyes. PBTC is not listed on the NTP, IARC or OSHA lists of carcinogenic substances. No toxic oral, mutagenic or teratogenic effects were observed in animal studies even at high doses. The LC_{50} for bacteria and rainbow trout were greater than 1000 mg/l and there were no harmful effects to daphnia at concentrations up to 300 mg/l. Elimination in a wastewater treatment plant is by flocculation with iron or aluminum salts. A removal mechanism similar to this in constructed wetlands is not readily apparent.

The acrylic acid telomer in the corrosion inhibitor is also not considered a carcinogen by NTP, IARC or OSHA. Biodegradability tests have not detected significant biodegradation. The 96 hour LC_{50} for bluegills and rainbow trout is over 1000 mg/l. The 48 hour daphnia LC_{50} is 1800 mg/l.

The biocide had a reported 6 day dynamic LC_{50} of 0.14 mg/l for rainbow trout. The 96 hour static LC_{50} for sheepshead minnows was reported as 0.3 mg/l.

Stormwater Quality

In 1983, EPA published the results of the National Urban Runoff Program (NURP) (EPA, 1983). The NURP study was composed of runoff water quality and quantity information from 28 reporting stations across the United States. The entire data base was analyzed in an attempt to correlate runoff quality and quantity with site characteristics, and provide guidance in estimating runoff quantity and quality and in assessing the deleterious effects to the environment. The

NURP data was thought to be representative of the expected range of runoff water quality from the Saturn plant because of the large size of the NURP data base.

In analyzing the NURP data, EPA showed that land use did not prove to be a useful basis for predicting runoff quality. Attempts at correlating quality with other parameters, including geographical location, was also unsuccessful. The storm event mean concentration (EMC) was reported and did not correlate with runoff volume. Flow weighted EMCs were reported where flow information was available. The EMCs were analyzed as log normal distributions. The standard pollutants measured consisted of total suspended solids (TSS), biochemical oxygen demand (BOD), chemical oxygen demand (COD), total phosphorous, soluble phosphorous, total Kjeldahl Nitrogen (TKN), nitrate-nitrogen, copper, lead and zinc. In addition, analyses for EPA priority pollutants were conducted at a number of sites.

Heavy metals were found to pose the most serious runoff quality problems. In particular, copper, lead and zinc were found in over 91% of events at maximum concentrations of 100, 460 and 2,400 micrograms per liter, respectively. The metals commonly violated water quality and drinking water standards. Freshwater acute toxicity for copper and lead were exceeded in 47% and 23% of events respectively. Freshwater chronic toxicity was exceeded for lead, copper, zinc and cadmium in 94%, 82%, 77% and 48% of the events, respectively. The most frequently detected heavy metal was lead which exceeded drinking water standards in 73% of events.

Of the EPA priority pollutants, 77 were detected, including 63 which were organic. The organic pollutants were detected less frequently and at lower concentrations than the metals. Coliform bacteria were present in high levels, and would be expected to exceed EPA standards frequently during and immediately after storm events in many surface waters, even those providing significant dilution. Warm weather also exacerbated coliform contamination, increasing up to twenty times during the summer.

Tabulated values for the median and 90th percentile EMC for the primary pollutants are presented in Chapter 4. The median was chosen as the representative value because it is less influenced by small numbers of relatively large values which are typical of a log normal distribution. Arsenic, nickel, lead, cyanides, cadmium, chromium, copper, zinc, chloroform, and napthalene are priority pollutants found in at least 10% of urban runoff samples and could be expected in stormwater runoff at the Saturn plant because of the parking lots and vehicular traffic. Source of these pollutants include gasoline and fossil fuel consumption/combustion, release from corrosion of plated surfaces, components of tires, road salt and asphalt, or other automobile related activities. Pesticides or other chemicals may be present, depending on their use at Saturn.

One of the most interesting conclusions of the NURP study was the effectiveness of wet detention basins in reducing pollutant concentrations in runoff. Particulate removals of greater than 90% for lead and TSS, 65% for phosphorous, and 50% for BOD, COD, TKN, copper and zinc were reported. Wet detention basins with permanent pools to support biological activity during dry periods were much more effective than dry detention basins in reducing pollutant loads. Constructed wetlands were also noted to show promise in treating runoff, though little actual design criteria was available. The NURP study did not observe that street sweeping seem to significantly reduced pollutant concentrations in runoff. However, Tschantz, et al. (1990) demonstrated through modeling that street sweeping could reduce pollutant concentrations in runoff.

Previous Saturn Studies

In 1986, Roy F. Weston, Inc. (Weston) prepared a study entitled "Feasibility Study of Land Application of Wastewater and Wastewater Sludges". The study investigated the Saturn plant site's soils, geology, etc. to determine if land application of biologically treated process wastes (not the cooling tower blowdown) was technically feasible and economical.

As a result of the study, spray irrigation was determined to be the optimum land application method. Soil analysis reported that the cation exchange capacity (CEC) of the Saturn site soils ranged from 5.4 - 17.1 meq/100 grams, which indicates potential for high metal application rates. Soil background levels of copper, zinc, cadmium, nickel, arsenic, mercury and selenium were also measured and were used in this investigation as discussed in Chapter 4 to calculate the potential for increasing soil metal levels over background.

The study attempted to determine limiting factors for spray irrigation. Nitrogen, phosphorous, and potassium applications were noted to be normally limited by contamination of surface and ground waters or crop fertilizer needs and were not considered to be the limiting pollutants for process wastes. Calcium and magnesium in process wastes were thought to be limiting only to the extent of influencing the sodium adsorption ratio (SAR). Long-term metal accumulations were found to be the limiting factor, unless pretreatment was practiced for metals removal. If pretreatment was practiced, hydraulic loading rates were thought to be the limiting factor. Land requirements for application of both pretreated and direct application of process wastes were determined.

The study concluded that approximately 500 acres of land at the Saturn site were technically suitable for land application of wastewaters. In addition to being technically feasible, preliminary cost analysis showed land application had economic advantages as well.

Chapter 3

EQUILIBRIUM MODELING

Equilibrium modeling was used to predict the concentration of the significant inorganic constituents of the blowdown water after treatment in a constructed wetlands filled with limestone media. The significant pollutants were identified as those above irrigation water quality standards as discussed in Chapter 4. The purpose of Chapter 3 is to discuss the background and methodology of the equilibrium modeling effort. The results of the equilibrium modeling, and the comparison of results to an operating constructed wetlands are presented and discussed in Chapter 4.

As discussed in Chapter 4, the inorganic pollutants of concern are copper, cadmium, bicarbonate, TDS and fluoride. The equilibrium modeling included precipitation and complexation equilibria. However, for the metals additional removal may be expected due to adsorption/ion exchange. Adsorption/ion exchange was not included in the modeling, however, because adequate treatment is accomplished for the metals by precipitation alone and, if adsorption/ion exchange were required to treat the blowdown water to irrigation limits, the long-term capacity of the wetlands would decrease as ion exchange/adsorption sites were filled.

The Minteq Geochemical Computer Model was used initially to model the blowdown effluent in equilibrium with solid calcium carbonate in the pH range of 7-11. The Minteq Geochemical Computer Model was written by the Pacific Northwest Laboratory (Pacific Northwest Laboratory, 1987). The Minteq model uses the thermodynamic principles to calculate precipitation , ion speciation, oxidation-reduction and gas phase equilibria. All of the projected blowdown constituents available in the Minteq model were included. Although the Minteq Model was sufficient to predict the expected effluent from the constructed wetlands, the code is quite complex to use and interpret. The Minteq model was not available for the personal computer to the author at that time, and had to be used on a main frame, which was expensive and time consuming. In order to generate a complete solubility curve for copper and cadmium, numerous Minteq runs would have been required (one for each pH increment), and a complete Minteq output for each full Saturn run is quite lengthy (over 10,000 lines).

As a result, a code was developed for this investigation to calculate total copper and cadmium concentrations in the pH range of 7-11. However, because calculated values of the effluent fluoride concentration did not change significantly above pH 8, Minteq was used for the small number of runs to calculate fluoride solubility between pH 7 - 8. Bicarbonate concentrations were also calculated by the code developed in this investigation. Minteq was used to identify constituents in the blowdown water which influence calculated copper and cadmium effluent concentrations, to identify significant complexes, and to check the accuracy of the model developed in this investigation. Calcium, carbonate, bicarbonate, sulfate, chloride and magnesium were identified as constituents in the blowdown water and constructed wetlands which would influence calculated effluent cadmium and copper concentrations. In general, concentrations of complexes in excess of 1% of total species concentration were considered significant. Solids to be considered were also selected by identification with the Minteq Model.

Equilibrium Modeling Assumptions

The following assumptions were used in the initial Minteq equilibrium modeling and in the development of the code for this investigation:

1. The final concentrations of all species are equilibrium concentrations and are not kinetically limited. The equilibrium assumption could introduce error in that when modeling precipitation phenomenon, the thermodynamically stable species may not form, due to kinetic limitations or inhibition of crystallization. The equilibrium assumption, however, is reasonable

because the residence time in a constructed wetlands is high, on the order of several days, and wetlands, especially subsurface flow wetlands (SFS), have tremendous surface area to promote crystallization.

2. The temperature was considered constant at 25^{o}C. Although equilibrium constants are temperature dependent, 25^{o}C was chosen as a representative temperature because the temperature is within the range of expected blowdown temperatures (Tschantz, et al ., 1990) and equilibrium modeling at 25^{o}C also matched the results reported from the Santee wetlands as discussed in Chapter 4. In addition, equilibrium constants and equilibrium modeling results are widely reported at 25^{o}C. The use of stormwater as a diluent, as discussed in Chapter 4, would reduce pollutant concentrations if treatment efficiency is reduced by temperature variations. However, the dependence of treatment efficiencies for inorganic pollutants on temperature is not known to have been reported in the literature.

3. The blowdown constituents with multiple possible oxidation states (including copper) were assumed to be in the highest oxidation state. The assumption is reasonable because the blowdown water is in a highly oxygenated environment and oxygen supply by plants is significant in a constructed wetlands as discussed in Chapter 2. The assumption is also conservative. Precipitation in the anoxic zone of a constructed wetlands (such as sulfide precipitation) is thought to be an important contributor to total metal removal (Gersberg, et al., 1984)

4. The solid copper hydroxide is allowed to precipitate rather than than the solid copper oxide, tenorite, which is the weathered form and is thought not to control precipitation equilibrium due to kinetic limitations. The assumption is also conservative because tenorite is less soluble than copper hydroxide.

5. The constructed wetlands is modeled as a closed system with respect to carbon dioxide (i.e. carbon dioxide is not allowed to transfer between the atmosphere and the constructed wetlands).

6. In the code developed in this investigation, the concentration of the copper and cadmium complex concentrations were taken as insignificant in comparison to the total chloride, sulfate and carbonate species to reduce the complexity of the code. Activity coefficients were also considered constant to reduce the complexity of the code. The goal of the assumptions was to introduce an error in the primary output parameter, the total metal concentration in the constructed wetlands effluent, of less than approximately 5%. Errors of this magnitude are certainly acceptable, because errors of at least 5% are common in measurements of equilibrium constants (Snoeyink and Jenkins, 1980). The accuracy of the code developed for this investigation will be validated by comparison to several Minteq runs as discussed later.

7. The constructed wetlands media for the SFS cells are limestone, $CaCO_3$, and the effluent water will be in equilibrium with $CaCO_3$. Dolomite, $CaMg(CO_3)_2$, under certain conditions of chemical composition and pH, is a more thermodynamically stable phase than limestone. Dolomite precipitation, however, was excluded from the equilibrium modeling because allowing dolomite to control copper and carbonate solubility rather than limestone would not be consistent with the actual physical conditions in the constructed wetlands, and the precipitation of dolomite from natural waters has not been observed and is not a controlling factor in calcium and carbonate equilibrium (Stumm and Morgan, 1981).

8. In the code developed in this investigation, copper and cadmium were modeled independently since they do not significantly affect each other so the number of constituents can be reduced considerably.

Equilibria and Mass Balance Equations

Equilibria Equations

For the metals of concern, copper and cadmium, the following reversible equilibria are important and were included in the code developed for this investigation (M represents the metal of concern, either Cu or Cd)

$$CaCO_3(s) \rightarrow Ca^{2+} + CO_3^{2-} \qquad (3\text{-}1)$$

$$H_2CO_3^* \rightarrow H^+ + HCO_3^- \qquad (3\text{-}2)$$

$$HCO_3^- \rightarrow H^+ + CO_3^{2-} \qquad (3\text{-}3)$$

$$M(OH)_2(s) \rightarrow M^{2+} + 2OH^- \qquad (3\text{-}4)$$

$$M_2(OH)_2CO_3(s) \rightarrow M^{2+} + 2OH^- + CO_3^{2-} \qquad (3\text{-}5)$$

$$MCO_3(s) \rightarrow M^{2+} + CO_3^{2-} \qquad (3\text{-}6)$$

$$M^{2+} + OH^- \rightarrow MOH^+ \qquad (3\text{-}7)$$

$$M^{2+} + 2OH^- \rightarrow MOH_2^0 \qquad (3\text{-}8)$$

$$M^{2+} + HCO_3^- \rightarrow MHCO_3^+ \tag{3-9}$$

$$M^{2+} + CO_3^{2-} \rightarrow MCO_3^0 \tag{3-10}$$

$$M^{2+} + SO_4^{2-} \rightarrow MSO_4^0 \tag{3-11}$$

$$M^{2+} + Cl^- \rightarrow MCl^+ \tag{3-12}$$

$$Ca^{2+} + HCO_3^- \rightarrow CaHCO_3^+ \tag{3-13}$$

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3^0 \tag{3-14}$$

$$Mg^{2+} + HCO_3^- \rightarrow MgHCO_3^+ \tag{3-15}$$

$$Mg^{2+} + CO_3^{2-} \rightarrow MgCO_3^0 \tag{3-16}$$

$$Ca^{2+} + SO_4^{2-} \rightarrow CaCO_4^0 \tag{3-17}$$

$$Mg^{2+} + SO_4^{2-} \rightarrow MgSO_4^0 \tag{3-18}$$

The equilibria equations describing the reactions are

$$\{Ca^{2+}\}\{CO_3^{2-}\} = K_{soCaCO_3} \tag{3-19}$$

$$\frac{\{H^+\}\,\{HCO_3^-\}}{\{H_2CO_3^*\}} = K_{a1} \qquad (3\text{-}20)$$

$$\frac{\{H^+\}\,\{CO_3^{2-}\}}{\{HCO_3^-\}} = K_{a2} \qquad (3\text{-}21)$$

$$\{M^{2+}\}\{OH^-\}^2 = K_{soM(OH)_2} \qquad (3\text{-}22)$$

$$\{M^{2+}\}^2\{OH^-\}^2\{CO_3^{2-}\} = K_{soM_2(OH)_2CO_3} \qquad (3\text{-}23)$$

$$\{M^{2+}\}\{CO_3^{2-}\} = K_{soMCO_3} \qquad (3\text{-}24)$$

$$\frac{\{MOH^+\}}{\{M^{2+}\}\,\{OH^-\}} = \beta_{MOH^+} \qquad (3\text{-}25)$$

$$\frac{\{MOH_2^0\}}{\{M^{2+}\}\,\{OH^-\}^2} = \beta_{M(OH)_2^0} \qquad (3\text{-}26)$$

$$\frac{\{MHCO_3^+\}}{\{M^{2+}\}\,\{HCO_3^-\}} = \beta_{MHCO_3^+} \qquad (3\text{-}27)$$

$$\frac{\{MCO_3^0\}}{\{M^{2+}\}\,\{CO_3^{2-}\}} = \beta_{MCO_3^0} \qquad (3\text{-}28)$$

$$\frac{\{MSO_4^o\}}{\{M^{2+}\}\{SO_4^{2-}\}} = \beta_{MSO_4^o} \qquad (3\text{-}29)$$

$$\frac{\{MCl^+\}}{\{M^{2+}\}\{Cl^-\}} = \beta_{MCl^+} \qquad (3\text{-}30)$$

$$\frac{\{CaHCO_3^+\}}{\{Ca^{2+}\}\{HCO_3^-\}} = \beta_{CaHCO_3^+} \qquad (3\text{-}31)$$

$$\frac{\{CaCO_3^o\}}{\{Ca^{2+}\}\{CO_3^{2-}\}} = \beta_{CaCO_3^o} \qquad (3\text{-}32)$$

$$\frac{\{MgHCO_3^+\}}{\{Mg^{2+}\}\{HCO_3^-\}} = \beta_{MgHCO_3^+} \qquad (3\text{-}33)$$

$$\frac{\{MgCO_3^o\}}{\{Mg^{2+}\}\{CO_3^{2-}\}} = \beta_{MgCO_3^o} \qquad (3\text{-}34)$$

$$\frac{\{CaSO_4^o\}}{\{Ca^{2+}\}\{SO_4^{2-}\}} = \beta_{CaSO_4^o} \qquad (3\text{-}35)$$

$$\frac{\{MgSO_4^o\}}{\{Ca^{2+}\}\{SO_4^{2-}\}} = \beta_{MgSO_4^o} \qquad (3\text{-}36)$$

where {i} = Activity of the ith species.

Table 3.1 lists the important equilibrium constants used in the development of the code.

The activity of the ith species is defined as (Snoeyink and Jenkins,1980)

$$\{i\} = \gamma_i \, [i] \qquad (3\text{-}37)$$

where γ_i = Activity coefficient of species i,

[i] = Molar concentration of species i (moles/l).

Activity coefficients can be expressed as functions of the ionic strength, which is a function of the ionic content of the water. Although the ionic content of the effluent water changes with pH, an average value of the activity coefficient for monovalent and divalent ions was calculated from the initial Minteq runs and used as a constant over all pH values. The average activity coefficients were calculated as

$$\gamma_1 = 0.895 \qquad (3\text{-}38)$$

$$\gamma_2 = 0.651 \qquad (3\text{-}39)$$

Activity coefficients as calculated by Minteq for monovalent ions varied from approximately 0.875 to 0.902. Activity coefficients for divalent ions varied from approximately 0.595 to 0.688.

Equations 3-19 through 3-36 can be rewritten in terms of molar concentrations rather than activities by combining the activity coefficients with the equilibrium constants to form a corrected equilibrium constant. Equations 3-40 through 3-57 written in terms of the corrected equilibrium are the equations used in the code.

Table 3.1 Equilibrium Constants[a]

Equilibrium Constant	Copper (log value)	Cadmium (log value)
K_{soCaCO_3}	-8.475	-8.475
$K_{soM(OH)_2}$	-19.36	-14.29
$K_{soM_2(OH)_2CO_3}$	-33.18	undefined[b]
K_{soMCO_3}	-9.63	-13.74
β_{MOH^+}	6.00	3.92
$\beta_{M(OH)_2^0}$	14.32	7.65
$\beta_{MHCO_3^+}$	2.67	2.07
$\beta_{MCO_3^o}$	6.73	5.40
$\beta_{MSO_4^o}$	2.31	2.46
β_{MCl^+}	0.43	1.98

---

a. Values of equilibrium constants calculated from the Minteq Geochemical Equilibrium Model.

b. Undefined indicates species does not exist.

$$[Ca^{2+}][CO_3^{2-}] = \frac{K_{soCaCO3}}{\gamma_{Ca^{2+}}\gamma_{CO_3^{2-}}} = {}^{c}K_{soCaCO3} \qquad (3\text{-}40)$$

$$\frac{[H^+][HCO_3^-]}{[H_2CO_3^*]} = \frac{\gamma_{H_2CO_3^*}K_{a1}}{\gamma_{H^+}\gamma_{HCO_3^-}} = {}^{c}K_{a1} \qquad (3\text{-}41)$$

$$\frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = \frac{\gamma_{HCO_3^-}K_{a2}}{\gamma_{H^+}\gamma_{CO_3^{2-}}} = {}^{c}K_{a2} \qquad (3\text{-}42)$$

$$[M^{2+}][OH^-]^2 = \frac{K_{soM(OH)2}}{\overset{2}{\gamma_{M^{2+}}}\overset{2}{\gamma_{OH^-}}} = {}^{c}K_{soM(OH)2} \qquad (3\text{-}43)$$

$$[M^{2+}]^2[OH^-]^2[CO_3^{2-}] = \frac{K_{soM2(OH)2CO3}}{\overset{2}{\gamma_{M^{2+}}}\overset{2}{\gamma_{OH^-}}\gamma_{CO_3^{2-}}} = {}^{c}K_{soM2(OH)2CO3} \qquad (3\text{-}44)$$

$$[M^{2+}][CO_3^{2-}] = \frac{K_{soMCO3}}{\gamma_{M^{2+}}\overset{2}{\gamma_{CO_3^{2-}}}} = {}^{c}K_{soMCO3} \qquad (3\text{-}45)$$

$$\frac{[MOH^+]}{[M^{2+}][OH^-]} = \frac{\gamma_{M^{2+}}\gamma_{OH^-}\beta_{MOH}}{\gamma_{MOH^+}} = {}^{c}\beta_{MOH^+} \qquad (3\text{-}46)$$

$$\frac{[MOH_2^0]}{[M^{2+}]\,[OH^-]^2} = \frac{\gamma_{M^{2+}}\,\gamma_{OH^-}^{2}\,\beta_{M(OH)2}}{\gamma_{MOH_2^0}} = {}^{c}\beta_{M(OH)_2^0} \qquad (3\text{-}47)$$

$$\frac{[MHCO_3^+]}{[M^{2+}]\,[HCO_3^-]} = \frac{\gamma_{M^{2+}}\,\gamma_{HCO_3^-}\,\beta_{MHCO_3^+}}{\gamma_{MHCO_3^+}} = {}^{c}\beta_{MHCO_3^+} \qquad (3\text{-}48)$$

$$\frac{[MCO_3^0]}{[M^{2+}]\,[CO_3^{2-}]} = \frac{\gamma_{M^{2+}}\,\gamma_{CO_3^{2-}}\,\beta_{MCO_3^0}}{\gamma_{MCO_3^0}} = {}^{c}\beta_{MCO_3^0} \qquad (3\text{-}49)$$

$$\frac{[MSO_4^0]}{[M^{2+}]\,[SO_4^{2-}]} = \frac{\gamma_{M^{2+}}\,\gamma_{SO_4^{2-}}\,\beta_{MSO_4^0}}{\gamma_{MSO_4^0}} = {}^{c}\beta_{MSO_4^0} \qquad (3\text{-}50)$$

$$\frac{\{MCl^+\}}{\{M^{2+}\}\,\{OH^-\}} = \frac{\gamma_{M^{2+}}\,\gamma_{Cl^-}\,\beta_{MCl}}{\gamma_{MCl^+}} = {}^{c}\beta_{MCl^+} \qquad (3\text{-}51)$$

$$\frac{[CaHCO_3^+]}{[Ca^{2+}]\,[HCO_3^-]} = \frac{\gamma_{Ca^{2+}}\,\gamma_{HCO_3^-}\,\beta_{CaHCO_3^+}}{\gamma_{CaHCO_3^+}} = {}^{c}\beta_{CaHCO_3^+} \qquad (3\text{-}52)$$

$$\frac{[CaCO_3^0]}{[Ca^{2+}]\,[CO_3^{2-}]} = \frac{\gamma_{Ca^{2+}}\,\gamma_{CO_3^{2-}}\,\beta_{CaCO_3^0}}{\gamma_{CaCO_3^0}} = {}^{c}\beta_{CaCO_3^0} \qquad (3\text{-}53)$$

$$\frac{[MgHCO_3^+]}{[Mg^{2+}]\,[HCO_3^-]} = \frac{\gamma_{Mg^{2+}}\,\gamma_{HCO_3^-}\,\beta_{MgHCO_3^+}}{\gamma_{MgHCO_3^+}} = {}^{c}\beta_{MgHCO_3^+} \qquad (3\text{-}54)$$

$$\frac{[MgCO_3^0]}{[Mg^{2+}]\,[CO_3^{2-}]} = \frac{\gamma_{Mg^{2+}}\,\gamma_{CO_3^{2-}}\,\beta_{MgCO_3^0}}{\gamma_{MgCO_3^0}} = {}^{c}\beta_{MgCO_3^0} \qquad (3\text{-}55)$$

$$\frac{[CaSO_4^0]}{[Ca^{2+}]\,[SO_4^{2-}]} = \frac{\gamma_{Ca^{2+}}\,\gamma_{SO_4^{2-}}\,\beta_{CaSO_4^0}}{\gamma_{CaSO_4^0}} = {}^{c}\beta_{CaSO_4^0} \qquad (3\text{-}56)$$

$$\frac{[MgSO_4^0]}{[Mg^{2+}]\,[SO_4^{2-}]} = \frac{\gamma_{Mg^{2+}}\,\gamma_{SO_4^{2-}}\,\beta_{MgSO_4^0}}{\gamma_{MgSO_4^0}} = {}^{c}\beta_{MgSO_4^0} \qquad (3\text{-}57)$$

Mass Balance Equations

In addition to the precipitation and complexation equilibrium equations, mass balance equations also govern equilibrium concentrations. The mass balance equations are

$$Ct_{CO_3} = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}] + [MHCO_3^+] + [MCO_3^0] +$$

$$[CaHCO_3^+] + [CaCO_3^0] + [MgHCO_3^+] + [MgCO_3^0] \qquad (3\text{-}58)$$

$$Ct_M = [M^{2+}] + [MOH^+] + [M(OH)_2^0] + [MHCO_3^+] + [MCO_3^0] + [MSO_4^0] \qquad (3\text{-}59)$$

$$Ct_{Ca} = [Ca^{2+}] + [CaHCO_3^+] + [CaCO_3^0] + [CaSO_4^0] \qquad (3\text{-}60)$$

$$Ct_{Mg} = [Mg^{2+}] + [MgHCO_3^+] + [MgCO_3^0] + [MgSO_4^0] \qquad (3\text{-}61)$$

$$Ct_{SO_4} = [SO_4^{2-}] + [CaSO_4^0] + [MgSO_4^0] + [MSO_4^0] \qquad (3\text{-}62)$$

$$Ct_{Cl} = [Cl^-] + [MCl^+] \qquad (3\text{-}63)$$

The following calcium and magnesium mass balances must also be realized when magnesium carbonate precipitates or calcium carbonate precipitates or dissolves

$$Ct_{Ca} = Ct0_{Ca} + S \qquad (3\text{-}64)$$

$$Ct_{Mg} = Ct0_{Mg} + P_{Mg} \qquad (3\text{-}65)$$

If a metal carbonate or metal hydroxide carbonate , i.e. $M_2(OH)_2CO_3$, precipitates, the total carbonate mass balance is

$$Ct_{CO_3} = Ct0_{CO_3} + S + P + P_{Mg} \qquad (3\text{-}66)$$

If a metal hydroxide precipitates, the total carbonate mass balance reduces to

$$Ct_{CO_3} = Ct0_{CO_3} + S + P_{Mg} \qquad (3\text{-}67)$$

The total metal mass balance is expressed as

$$Ct_M = Ct0_M + P \qquad (3\text{-}68)$$

if the solid metal hydroxide or metal carbonate is precipitated. If the solid metal hydroxide carbonate , i.e. $M_2(OH)_2CO_3$, precipitates, the governing mass balance equation becomes

$$Ct_M = Ct0_M + 2P \qquad (3\text{-}69)$$

where Ct_i = Total amount of species i in solution (moles/liter),

$Ct0_i$ = Total amount of species i originally in solution (moles/liter),

S = Amount of $CaCO_3$ precipitating or dissolving (moles/l),

P = Amount of solid metal phase precipitating (moles/l),

P_{Mg} = Amount of solid magnesium carbonate precipitating (moles/l).

Code Construction

The code developed for this investigation was written in True Basic on the Macintosh II and is shown in Appendix 1. The program operates by an iterative method to calculate final effluent concentrations. The iterative method operates by supplying a value of the calcium ion concentration, which reduces the number of equations necessary to solve the equilibrium problem by one. The program then sequentially calculates the values of all the other species in equilibrium with the supplied calcium ion concentration.

The test for convergence is defined as the difference function (the difference function is the relative difference between the two sides of the equation chosen by the author which was not required to solve the equilibrium problem because the calcium ion concentration was supplied.) In the subroutines for precipitating the metal hydroxide, metal carbonate, and the metal hydroxide carbonate, the equations used for the difference function were equations 3-67, 3-45 and 3-44 respectively. The two sides of the equation are calculated sequentially from the supplied calcium ion concentration. If the difference function is less than the defined error criteria, the calcium ion concentration supplied by the program was correct, as well as all concentrations calculated from the value, and the program has reached a solution. The error criteria was chosen by the author as 1E-6 after some test runs. If the difference function is larger than the defined error criteria, a new value of the calcium ion concentration is supplied by the program in a new iteration. The change in sign of the difference function also indicates when the program has passed the solution (the correct value of the calcium ion concentration), refining the next iteration's supplied calcium ion concentration value.

To validate the code developed for this investigation, the results were compared to several Minteq runs. A comparison of the code's calculated values of the total effluent metal concentration for copper and cadmium with values from Minteq is shown in Tables 3.2 and 3.3. An abbreviated representative Minteq run (the input and final output values are listed without the intermediate values printed during the iterative process) is shown in Appendix 2.

Table 3.2 Calculated Values of Effluent Cadmium Concentration versus Values from Minteq

pH	Calculated CtCd (moles/liter)	Minteq CtCd (moles/liter)	Percent Difference
7	2.74e-8	2.75e-8	+0.4
8	7.67e-9	7.50e-9	-2.2
9	5.11e-9	4.98e-9	-2.5
10	4.78e-9	4.66e-9	-2.5
11	5.38e-9	5.29e-9	-1.7

Table 3.3 Calculated Values of Effluent Copper Concentration versus Values from Minteq

pH	Calculated CtCu (moles/liter)	Minteq CtCu (moles/liter)	Percent Difference
7	3.20e-6	3.23e-6	+0.9
8	1.91e-6	1.93e-6	+1.0
9	5.24e-6	5.18e-6	-1.1
10	9.13e-6	9.14e-6	+0.1
11	9.12e-6	9.15e-6	+0.3

Chapter 4

RESULTS AND DISCUSSION

The principle objective of this investigation, as discussed in Chapter 1, is to assess the potential for using constructed wetlands followed by spray irrigation of crops to successfully and safely treat the blowdown water. In assessing the fate and effect of the inorganic constituents in the system (the constructed wetlands and wastewater irrigation system), an acceptable concentration limit will be determined by comparison of projected blowdown water quality with irrigation water quality standards which have been developed for wastewater irrigation. For the inorganic constituents actually expected in excess of irrigation water quality standards, the expected degree of treatment in the constructed wetlands will be calculated from precipitation and complexation equilibrium modeling. To assess the validity of the equilibrium modeling approach, a comparison of calculated effluent metal concentrations with results reported from an operating constructed wetlands will also be performed. The potential for deleterious buildup of metals in the crop soil will be calculated. The quality of site stormwater runoff will also be assessed for use as a diluent for those constituents not projected to receive adequate treatment in the constructed wetlands.

The fate and effect of the organic constituents of the blowdown water will be determined by a review of the literature and information provided by the manufacturer (as discussed in Chapter 2). The degree of treatment expected in the constructed wetlands and crop soils will be estimated, where possible, from a correlation with a measured or estimated value of the chemical's octanol/water partition coefficient, a predictor of environmental fate. A conceptual design and cost estimate of the constructed wetlands will also be performed.

Projected Blowdown Water Quality and Quantity

Water Quality

The cooling tower blowdown water quality is a function of city water quality used in the cooling system, the evaporative losses during operations of the cooling tower and the addition of a corrosion inhibitor and biocide. The concentrations of pollutants contributed by the city water are simply the water quality characteristics of the city water concentrated by the number of cycles of concentrations, i.e. evaporation in the tower. Both a three and five cycle scenario was being considered by Saturn, but for this study the five cycle scenario was used because the contaminants were more concentrated. In other words, the five cycle scenario was considered as the worst case in terms of pollutant concentration of the two scenarios considered. The cooling tower blowdown water quality was supplied by Saturn, based on city water analysis (i.e. five times the city's tap water concentration) performed by Dexter Chemical. The projected blowdown water quality for the five cycle assumption is shown in Table 4.1. The constituents, listed as less than a concentration value, are listed as five times the minimum detectable concentration in city water. The actual concentrations may be significantly less than the stated values.

The chemicals contributed by the biocide and the corrosion inhibitor are shown in Table 4.2. The concentrations for the chemicals contributed by the corrosion inhibitor are the expected values. Concentrations for the biocide are not listed, as the biocide will only be used for shock treatment.

Water Quantity

Blowdown rates could be as high as 72 million gallons per year operating in the 3 cycle scenario (fewer tower cycles require more water). The peak summer blowdown rate could be as high as 736,000 gallons per day with a summer average of approximately 464,000 gallons per

Table 4.1 Projected Blowdown Water Quality

Component	Concentration (mg/l)
Silica	2
Total Organic Carbon	77
Total Dissolved Solids	1116
Sulfate	290
Chloride	50
Carbonate	5
Bicarbonate	712
Nitrogen-Nitrate	4
Fluoride	5
Phosphates-Total	2
Hardness (as $CaCO_3$)	590
Alkalinity (as $CaCO_3$)	720
Calcium	320
Magnesium	28
Iron	0.03
Manganese	<0.025
Beryllium	<0.005
Copper	0.7
Nickel	<0.025
Aluminum	1.6
Sodium	64
Potassium	6.5
Antimony	<0.025
Cadmium	<0.025
Chromium-Total	<0.025
Lead	0.04
Mercury	<0.001
Selenium	<0.005
Silver	<0.025
Thallium	<0.025
Zinc	<0.025
Arsenic	<0.005
Turbidity	1 NTU
pH	7.8

a. Based on 5 cycle concentration assumption

b. The constituents listed as less than a value are listed as five times the minimum detectable concentration in city water. The actual concentrations may be significantly less than the stated values.

Table 4.2 Organic Constituents Contributed by the Corrosion Inhibitor and Biocide

Component	Concentration (mg/l)
Corrosion Inhibitor, Mogul 11215	
Sodium Hydroxide	Included in Table 4.1
Tolytriazole CAS No. 29385-43-1	1.6
1-Hydroxyethylidene-1,1-diphosphonic acid CAS No. 2809-21-4	1.7
Acrylic acid, telomer with sodium 2-acrylamido-2-methyl-1-propane sulfonate and sodium phosphinate CAS No. 110224-99-2	3.0
2-phosphonobutane-1,2,4-tricarboxylic acid CAS No. 37971-36-1	1.6
Biocide, Mogul AG-480	
Copper Nitrate Trihydrate CAS No. 3251-23-8	Varies[a]
Chloro-2-methyl-4-isothiazolin-3-one CAS No. 26172-55-4	Varies[a]
2-methyl-4-isothiazolin-3-one CAS No. 2682-20-4	Varies[a]

a. The concentration of the biocide will vary due to use as a shock treatment.

day. The winter blowdown rates are significantly lower, peaking at 67,000 gallons per day and averaging 45,000 gallons per day. A detailed assessment of the expected flow rates performed by Saturn is shown in Table 4.3.

Projected Stormwater Quality

The projected stormwater quality was obtained from the National Urban Runoff Program Study as discussed in Chapter 2. Tabulated values for the median and 90th percentile EMC (Event Mean Concentration) for the primary pollutants are shown in Table 4.4.

Fate of the Inorganic Blowdown Water Constituents in the System

Assessing the impact of specific pollutants on crops, soils and the food chain is complex. Each pollutant may be of concern for a variety of reasons. Pollutants may be directly toxic to the crops, may accumulate to unacceptable levels in the soil, or the plants may absorb and concentrate the pollutants to such an extent that introduction into the food chain is unsafe. Complicating the situation is the fact that different crops have widely varying tolerances and uptakes of individual pollutants. Differences in soil characteristics may also influence the effect of individual pollutants.

Irrigation Water Quality Standards

As an aid in assessing the fate and effect of inorganic wastewater constituents during irrigation, a number of irrigation water quality standards have been developed. These irrigation water quality standards are based on the most likely damaging effect of a given pollutant and the most sensitive plant species. In some cases, soil characteristics are considered in establishing limits for pollutant buildup in soils. In most instances, the limiting pollutant concentration is based on introduction of pollutants into the food chain.

Table 4.3 Projected Blowdown Water Quantity

Season	3 Cycle Flow (gal/day)	5 Cycle Flow (gal/day)
Winter Peak	67,000	33,000
Winter Average	45,000	22,000
Winter Minimum	0	0
Spring Peak	192,000	95,000
Spring Average	140,000	71,000
Spring Minimum	7,000	4,000
Summer Peak	736,000	295,000
Summer Average	464,000	232,000
Summer Minimum	104,000	52,000
Fall Peak	220,320	111,000
Fall Average	163,000	81,000
Fall Minimum	7,000	4,000
Annual Volume(gallons)	72,600,000	36,300,000

Table 4.4 Median and 90th Percentile Values of Standard Pollutants from NURP

Pollutant	Site Median EMC (mg/l)	Site 90th Percentile EMC (mg/l)
TSS	100	300
BOD	9	15
COD	65	140
Total P	0.33	0.70
Soluble P	0.12	0.21
TKN	1.50	3.30
Nitrate-N	0.68	1.75
Copper	0.034	0.093
Lead	0.144	0.350
Zinc	0.160	0.500

a. EMC = Event Mean Concentration

The irrigation water quality standards presented herein are considered safe for long-term irrigation of all plant species under normal conditions. Exceeding these limits for short periods or increasing the limit for certain situations is not necessarily unfavorable, and exceptions may be warranted for individual cases.

As a result of the comparison of blowdown water quality with irrigation water quality limits, the pollutants in the blowdown water have been divided into three categories: those with concentrations below irrigation water quality standards, those with concentrations above irrigation water quality standards, and those with unknown irrigation limits. The three categories are shown in Tables 4.5 - 4.7. The irrigation standards include those promulgated by Tennessee Department of Health and Environment (TDHE) and those typical of the values recommended in the literature.

Pollutants which are present in concentrations below irrigation water quality standards are considered safe, with no further assessment of fate in the system warranted. The pollutants without irrigation water quality standards were also considered safe in an earlier study (Tschantz, et al., 1990) without further consideration of overall fate . In addition, mercury is actually not expected to exceed the limits because the projected blowdown concentration is just marginally above the irrigation limit recommended in the literature (no limit has been established by TDHE) and the projected blowdown concentration is 5 times the detection limit, rather than the actual concentration. The actual mercury concentration is expected to be less than the irrigation limit directly from the tower. Therefore, only the pollutants actually expected in excess of water quality limits, TDS, bicarbonate, fluoride, copper and cadmium and those contributed by the corrosion inhibitor and biocide require further investigation for their behavior in the system.

Table 4.5 Pollutants with Expected Concentrations Below Irrigation Water Quality Limits

Pollutant	Concentration (mg/l)	Irrigation Limit (mg/l)[a]	TDHE Limit (mg/l)[b]
Chloride	50	100	100
Nitrogen-N	0.9	5	
pH	7.8	6.5-8.4	6.5-8.4
Iron	0.03	5	10
Manganese	<0.025	0.2	0.4
Beryllium	<0.005	0.1	0.2
Nickel	<0.025	0.2	0.4
Aluminum	1.6	5	10
Chromium	<0.025	0.1	0.2
Lead	0.04	5	10
Selenium	<0.005	0.02	0.04
Zinc	<0.025	2	4
Arsenic	<0.005	0.1	0.2
SAR	1	3	5
Sodium	64	70	70
Silver	<0.025	4	

a. Irrigation Limit from Wescot, D. W. and R. S. Ayers. "Irrigation Water Quality Criteria" In: Irrigation with Reclaimed Municipal Wastewater, Lewis Publishers, Chelsea, MI. 1985.

b. TDHE Limit from Tennessee Department of Health and Environment, Chapter 16, Slow Rate Land Treatment in Design Criteria of Sewage Treatment Works.

Table 4.6 Pollutants With Expected Concentrations Above Irrigation Water Quality Limits

Pollutant	Concentration (mg/l)	Irrigation Limit (mg/l)[a]	TDHE Limit (mg/l)[b]
TDS	1166	500[c]	Not established
Bicarbonate	712	90[d]	91[e]
Fluoride	5	1	1.8
Copper	0.7	0.2	0.4
Mercury	<0.001	0.0009	Not established
Cadmium	<0.025	0.01	0.02

a. Irrigation Limit from Wescot, D. W. and R. S. Ayers. "Irrigation Water Quality Criteria" In: Irrigation with Reclaimed Municipal Wastewater, Lewis Publishers, Chelsea, MI. 1985.

b. TDHE Limit from Tennessee Department of Health and Environment, Chapter 16, Slow Rate Land Treatment in Design Criteria of Sewage Treatment Works.

c. Limit is defined as <500 no restrictions, 500-2000 slight to moderate restrictions, >2000 severe restrictions.

d. Limit is defined as <90 no restrictions, 90-500 slight restrictions, >500 severe restrictions.

e. Limit is defined as <91 no problem, 91-519 increasing problems, >519 severe problems.

Table 4.7 Pollutants With Unknown Irrigation Limits

Pollutant	Concentration (mg/l)
Silica	2
TOC	77
Phosphates	2
Potassium	6.5
Carbonate	5
Turbidity	1 NTU
Hardness (as $CaCO_3$)	590
Alkalinity (as $CaCO_3$)	720
Calcium	320
Magnesium	28
Antimony	<0.025
Sulfate	290
Thallium	<0.025

In addition, the concentrations of TDS and bicarbonate are not considered as restrictive because of the comparatively flexible definition of the limits and low toxicity. On a scale of no restrictions, slight restrictions and severe restrictions, TDS is in the middle category directly from the cooling tower. The blowdown water is also oversaturated with calcium carbonate, as discussed later, and precipitation will reduce the bicarbonate concentrations by at least 50% to the middle category. Neither pollutant was thought to pose severe toxicity, either to plants or consumers (Tschantz, et al., 1990). As a result, TDS and bicarbonate in excess of irrigation limits is considered a management problem which can be controlled.

Potential for Deleterious Metal Buildup in Crop Soil

Irrigation with water as good or better than the irrigation water quality limits should not pose a problem for prolonged irrigation, including metal accumulations. The TDHE regulations for the land application of sewage sludges (TDHE, 1987) does list maximum site metal accumulations based on soil cation exchange capacity (CEC). Although the applicability of the sludge regulation to wastewater irrigation is not clear, the maximum metal input to the crop soil from irrigation with untreated blowdown water was calculated to verify that no problems would be expected. Table 4.8 lists 1. the maximum allowable lifetime accumulation limits for metals as listed in the TDHE regulations for the land application of sewage sludges, 2. the annual inputs for irrigation with untreated blowdown water, and 3. the resultant time required to exceed the accumulation limits. After treatment in a constructed wetlands, metal concentrations will be lower than the effluent blowdown water quality. However, the soil buildup was calculated from untreated blowdown water as a worst case. Cadmium has the shortest time required to exceed the accumulation limits, with 19 years, so long-term metal accumulation does not seem to be a problem. However, irrigation with untreated blowdown water could increase soil background metal content.

Table 4.8 Time Required to Exceed Maximum Accumulation Limits

Metal	Lifetime Limit[a] (kg/ha)	Application Rate[b] (kg/ha/year)	Years to Exceed
Lead	1000	0.5	2000
Zinc	500	0.3	1667
Copper	250	8.4	30
Nickel	100	0.3	333
Cadmium	5.6	0.3	19

a. Tennessee Department of Health and Environment, Division of Water Pollution Control, Guidelines for Land Application of Municipal Sludge, 1987. Accumulation limits based on soil CEC of 5-15 meq/100 grams.

b. Application rates are based on irrigation at 4 ft/year with untreated blowdown water.

Table 4.9 lists background levels of metals in the soil, the expected metals addition after twenty years of irrigation with untreated blowdown water, and the resultant percentage increase in soil metal content. Copper, cadmium, and selenium would all be significantly increased above soil background levels, but would still not exceed TDHE sludge application guidelines for at least 19 years. The actual cadmium and selenium increases may be much less because the blowdown concentration used for this analysis is five times the minimum detectable concentration in the city water, and not the actual expected concentration.

Projected Treatment in the Constructed Wetlands

For the inorganic constituents of the blowdown water in excess of established irrigation standards, equilibrium modeling by the methodology described in Chapter 3 was used to predict the degree of treatment in a constructed wetlands due to precipitation.

As discussed previously, metal removal in a constructed wetlands occurs primarily by adsorption/ion exchange and precipitation though the relative contribution of each is unknown. However, if metal removal occurs by adsorption/ion exchange, the ultimate capacity of the constructed wetlands may be limited due to exhaustion of exchange sites, and the ultimate capacity is unknown. If metal removal occurs primarily by precipitation, the capacity of the constructed wetlands should be much less limited. The equilibrium modeling did not include adsorption/ion exchange but considered only precipitation and complexation. Therefore metal removal calculated to occur by precipitation is expected to occur indefinitely, and the capacity of the constructed wetlands to treat the blowdown water can be considered essentially unlimited.

Of the inorganic pollutants exceeding irrigation water quality criteria, only TDS, bicarbonate, copper, cadmium and fluoride are considered significant. TDS and bicarbonate, as discussed earlier, are considered management problems rather than environmental problems due to the

Table 4.9 Metal Accumulation in Soils after Twenty Years

Metal	Background[a] (kg/ha)	Addition After Twenty Years[b] (kg/ha)	% Increase
Zinc	243	6	2
Copper	72	168	233
Nickel	99	6	6
Cadmium	2.25	6	267
Arsenic	45	1.2	3
Selenium	0.36	1.2	333

a. Background levels from Saturn's Feasibility Study for the Land Application of Wastewater and Wastewater Sludges (Weston, 1986). Conversion from background levels in the laboratory to kilograms per hectare from Wescot and Ayers, 1985.

b. Application rates are based on irrigation at 4 ft/yr with untreated blowdown water.

nature of the definition of the limit. Equilibrium modeling was used to calculate effluent inorganic constituent concentrations.

The calculated effluent concentrations of inorganic constituents are functions of effluent pH. Many factors influence the pH of constructed wetlands effluent. Typically average changes in pH from influent to effluent are small. Constructed wetlands often increase pH (Watson, et al., 1989), though many influent pH values reported in the literature are acidic .

The pH of the Saturn blowdown water is 7.8 directly from the cooling tower. The pH of the blowdown water in equilibrium with calcium carbonate was calculated by Minteq as 10.6. Therefore, from equilibrium calculations only, the pH would increase from influent to effluent. To include the theoretical equilibrium pH, equilibrium modeling was conducted for the constructed wetlands effluent pH range of 7-11, though the actual effluent pH from the Saturn constructed wetlands is typically expected to vary from approximately pH 7 - 8.5. The effluent pH is not expected to typically exceed 8.5, because average effluent pH values above approximately this level are outside the range of values reported in the literature. The effluent pH is not typically expected to decrease below pH 7, because constructed wetlands have been used to neutralize acidic wastewaters (Gersberg, et al., 1984). Effluent pH outside this range will begin to sacrifice copper and cadmium removal efficiencies based on equilibrium calculations. Use of stormwater as a diluent, as discussed later, would provide protection against increased copper and cadmium concentrations in the effluent due to larger changes in pH from influent to effluent.

Cadmium

The calculated effluent cadmium concentrations based on equilibrium modeling were well below the TDHE irrigation limit of 20 micrograms/l throughout the entire pH range. Effluent cadmium concentrations varied with effluent pH, ranging from 0.6 micrograms/l to 3.1 micrograms/l. The stable solid phase for the entire range is cadmium carbonate. Figure 4.1 shows the effluent cadmium concentration versus pH as well as the TDHE irrigation limit.

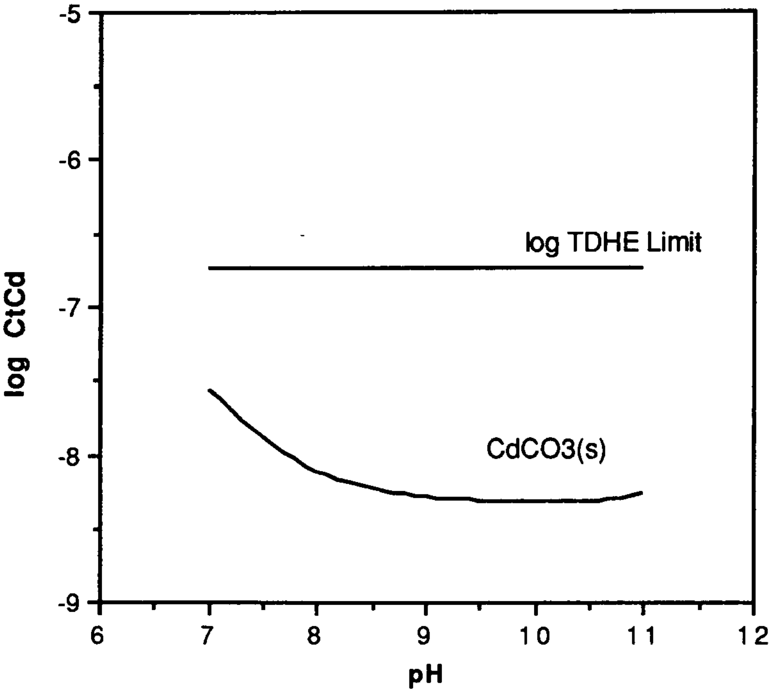


Figure 4.1 Effluent Cadmium Concentration versus pH

Figure 4.2 shows the cadmium complexation for the significant complexes over the pH range. Table 4.10 shows the calculated values of the total cadmium concentration as well as the individual cadmium complex concentrations.

Copper

The calculated effluent copper concentrations based on equilibrium modeling were well below the TDHE limit of 0.4 mg/l for the expected effluent pH range. Figure 4.3 shows the total effluent copper concentration versus pH as well as the TDHE limit. Figure 4.4 show the total concentration of copper in equilibrium with the solid phases malachite ($Cu_2(OH)_2CO_3$) and copper hydroxide over the pH range. Below pH 9.5 solid malachite is the stable phase. Above pH 9.5 copper hydroxide is the stable solid phase. Figure 4.5 shows the individual copper complex concentrations versus pH. Table 4.11 shows the calculated values of the total copper concentrations as well as the individual copper complex concentrations.

Fluoride

Initial modeling with the Minteq geochemical equilibrium model indicated that fluoride will not be reduced below the TDHE irrigation limit as a result of precipitation in the constructed wetlands at the expected range of effluent pH. However, calculated values of the fluoride effluent concentration indicate fluoride could be reduced by precipitation of fluorite (CaF_2) to 2.0 mg/l at pH 7, although the effluent is still above the TDHE irrigation limit of 1.8 mg/l. Calculated values of the fluoride effluent concentration continue to increase to an approximately constant level of 4.8 mg/l above pH 8.

Bicarbonate

Levels of bicarbonate in the constructed wetlands effluent are, of course, highly pH dependent, with higher levels of bicarbonate associated with lower pH values. In all cases, however, the level of bicarbonate calculated by equilibrium modeling decreased significantly from the blowdown concentration of 712 mg/l. Bicarbonate levels were calculated by the model to be reduced by at least 50% to 329 mg/l at pH 7 which is in the middle restriction category. Higher

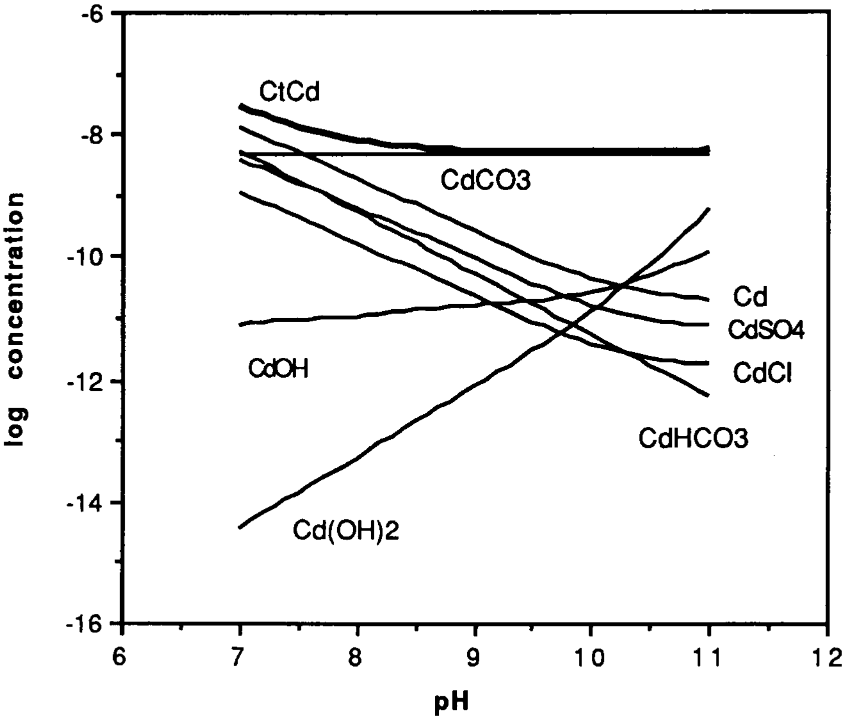


Figure 4.2 Effluent Cadmium Complex Concentrations

Table 4.10 Cadmium Complex Concentrations

pH	CtCd (moles/liter)	Cd (moles/liter)	CdOH (moles/liter)	Cd(OH)2 (moles/liter)	CdHCO3 (moles/liter)	CdCO3 (moles/liter)	CdSO4 (moles/liter)	CdCl (moles/liter)
7.0	2.738e-08	1.267e-08	7.664e-12	3.684e-15	5.226e-09	4.677e-09	3.687e-09	1.110e-09
7.1	2.336e-08	1.047e-08	7.974e-12	4.825e-15	4.151e-09	4.677e-09	3.132e-09	9.177e-10
7.2	2.003e-08	8.642e-09	8.287e-12	6.313e-15	3.297e-09	4.677e-09	2.647e-09	7.576e-10
7.3	1.728e-08	7.121e-09	8.596e-12	8.244e-15	2.619e-09	4.677e-09	2.225e-09	6.242e-10
7.4	1.500e-08	5.855e-09	8.897e-12	1.074e-14	2.081e-09	4.677e-09	1.861e-09	5.132e-10
7.5	1.311e-08	4.800e-09	9.184e-12	1.396e-14	1.653e-09	4.677e-09	1.548e-09	4.208e-10
7.6	1.155e-08	3.925e-09	9.454e-12	1.809e-14	1.313e-09	4.677e-09	1.281e-09	3.441e-10
7.7	1.026e-08	3.200e-09	9.702e-12	2.337e-14	1.043e-09	4.677e-09	1.055e-09	2.805e-10
7.8	9.210e-09	2.601e-09	9.929e-12	3.011e-14	8.283e-10	4.677e-09	8.648e-10	2.280e-10
7.9	8.345e-09	2.109e-09	1.013e-11	3.869e-14	6.579e-10	4.677e-09	7.061e-10	1.849e-10
8.0	7.676e-09	1.730e-09	1.046e-11	5.029e-14	5.226e-10	4.677e-09	5.844e-10	1.516e-10
8.1	7.180e-09	1.452e-09	1.106e-11	6.692e-14	4.151e-10	4.677e-09	4.974e-10	1.273e-10
8.2	6.760e-09	1.214e-09	1.164e-11	8.868e-14	3.297e-10	4.677e-09	4.209e-10	1.064e-10
8.3	6.405e-09	1.011e-09	1.221e-11	1.171e-13	2.619e-10	4.677e-09	3.541e-10	8.863e-11
8.4	6.107e-09	8.387e-10	1.275e-11	1.539e-13	2.081e-10	4.677e-09	2.963e-10	7.352e-11
8.5	5.857e-09	6.931e-10	1.326e-11	2.016e-13	1.653e-10	4.677e-09	2.467e-10	6.076e-11
8.6	5.648e-09	5.709e-10	1.375e-11	2.631e-13	1.313e-10	4.677e-09	2.045e-10	5.004e-11
8.7	5.475e-09	4.688e-10	1.422e-11	3.424e-13	1.043e-10	4.677e-09	1.688e-10	4.110e-11
8.8	5.332e-09	3.841e-10	1.466e-11	4.447e-13	8.283e-11	4.677e-09	1.389e-10	3.367e-11
8.9	5.215e-09	3.142e-10	1.510e-11	5.766e-13	6.579e-11	4.677e-09	1.141e-10	2.755e-11
9.0	5.119e-09	2.569e-10	1.554e-11	7.471e-13	5.226e-11	4.677e-09	9.355e-11	2.252e-11
9.1	5.041e-09	2.101e-10	1.600e-11	9.683e-13	4.151e-11	4.677e-09	7.669e-11	1.842e-11
9.2	4.978e-09	1.720e-10	1.650e-11	1.257e-12	3.297e-11	4.677e-09	6.292e-11	1.508e-11
9.3	4.928e-09	1.412e-10	1.705e-11	1.635e-12	2.619e-11	4.677e-09	5.173e-11	1.238e-11
9.4	4.887e-09	1.163e-10	1.768e-11	2.134e-12	2.081e-11	4.677e-09	4.268e-11	1.020e-11
9.5	4.855e-09	9.632e-11	1.843e-11	2.801e-12	1.653e-11	4.677e-09	3.537e-11	8.443e-12

Table 4.10 (Continued)

pH	CtCd (moles/liter)	Cd (moles/liter)	CdOH (moles/liter)	Cd(OH)2 (moles/liter)	CdHCO3 (moles/liter)	CdCO3 (moles/liter)	CdSO4 (moles/liter)	CdCl (moles/liter)
9.6	4.830e-09	8.025e-11	1.933e-11	3.698e-12	1.313e-11	4.677e-09	2.949e-11	7.034e-12
9.7	4.811e-09	6.737e-11	2.043e-11	4.921e-12	1.043e-11	4.677e-09	2.478e-11	5.906e-12
9.8	4.797e-09	5.707e-11	2.179e-11	6.607e-12	8.283e-12	4.677e-09	2.100e-11	5.003e-12
9.9	4.787e-09	4.885e-11	2.347e-11	8.962e-12	6.579e-12	4.677e-09	1.798e-11	4.282e-12
10.0	4.782e-09	4.228e-11	2.558e-11	1.230e-11	5.226e-12	4.677e-09	1.557e-11	3.706e-12
10.1	4.781e-09	3.705e-11	2.822e-11	1.708e-11	4.151e-12	4.677e-09	1.365e-11	3.248e-12
10.2	4.784e-09	3.288e-11	3.153e-11	2.402e-11	3.297e-12	4.677e-09	1.212e-11	2.882e-12
10.3	4.793e-09	2.956e-11	3.569e-11	3.422e-11	2.619e-12	4.677e-09	1.090e-11	2.591e-12
10.4	4.809e-09	2.692e-11	4.091e-11	4.940e-11	2.081e-12	4.677e-09	9.923e-12	2.360e-12
10.5	4.835e-09	2.482e-11	4.749e-11	7.218e-11	1.653e-12	4.677e-09	9.150e-12	2.176e-12
10.6	4.875e-09	2.315e-11	5.576e-11	1.067e-10	1.313e-12	4.677e-09	8.535e-12	2.029e-12
10.7	4.936e-09	2.182e-11	6.617e-11	1.594e-10	1.043e-12	4.677e-09	8.046e-12	1.913e-12
10.8	5.028e-09	2.077e-11	7.927e-11	2.404e-10	8.283e-13	4.677e-09	7.657e-12	1.820e-12
10.9	5.168e-09	1.993e-11	9.576e-11	3.656e-10	6.579e-13	4.677e-09	7.348e-12	1.747e-12
11	5.383e-09	1.926e-11	1.165e-10	5.601e-10	5.226e-13	4.677e-09	7.102e-12	1.688e-12

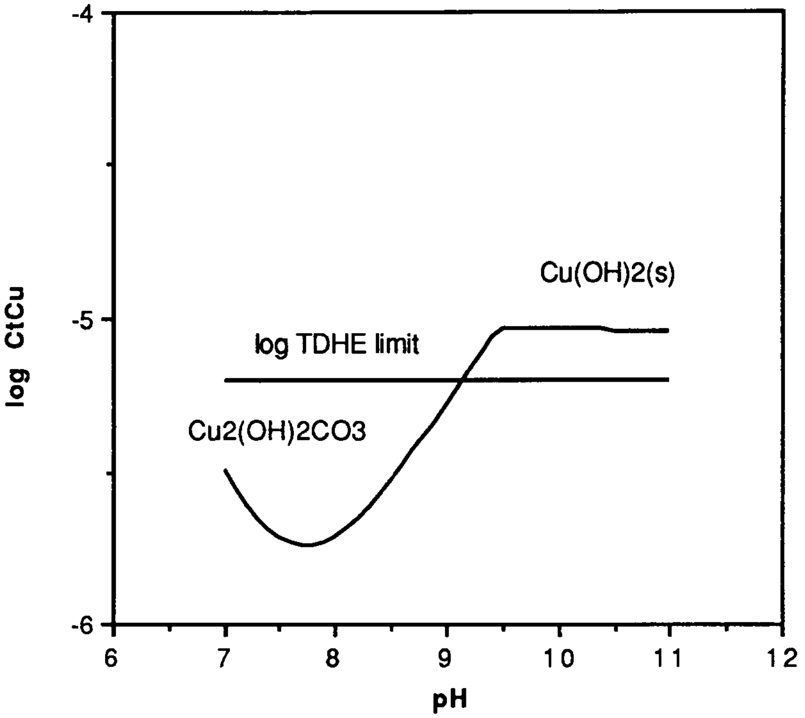


Figure 4.3 Effluent Copper Concentration versus pH

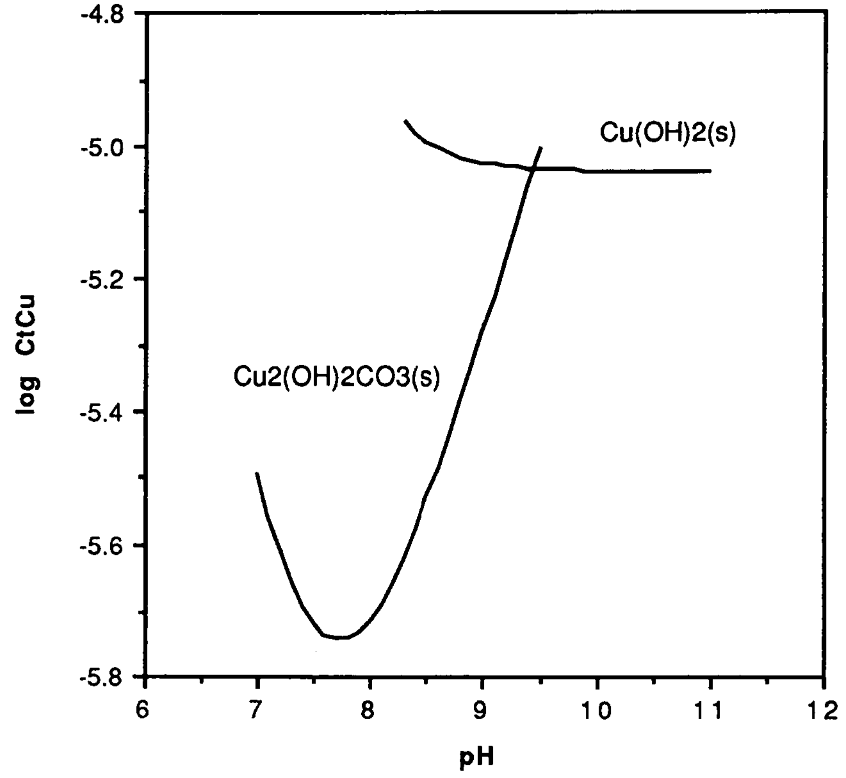


Figure 4.4 Solid Copper Phase Diagram

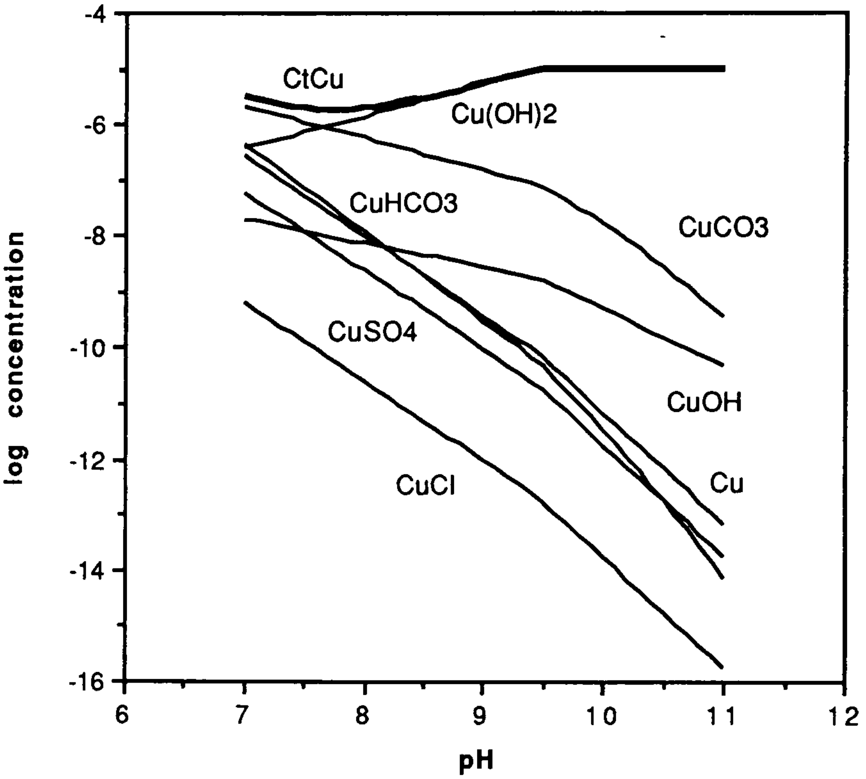


Figure 4.5 Effluent Copper Complex Concentrations

Table 4.11 Copper Complex Concentrations

pH	CtCu (moles/liter)	Cu (moles/liter)	CuOH (moles/liter)	Cu(OH)2 (moles/liter)	CuHCO3 (moles/liter)	CuCO3 (moles/liter)	CuSO4 (moles/liter)	CuCl (moles/liter)
7.0	3.200e-06	2.628e-07	1.912e-08	3.575e-07	4.315e-07	2.074e-06	5.415e-08	6.493e-10
7.1	2.768e-06	1.898e-07	1.738e-08	4.091e-07	2.995e-07	1.812e-06	4.020e-08	4.689e-10
7.2	2.443e-06	1.370e-07	1.579e-08	4.680e-07	2.079e-07	1.584e-06	2.970e-08	3.384e-10
7.3	2.201e-06	9.877e-08	1.433e-08	5.348e-07	1.445e-07	1.386e-06	2.185e-08	2.440e-10
7.4	2.026e-06	7.114e-08	1.300e-08	6.105e-07	1.006e-07	1.214e-06	1.601e-08	1.758e-10
7.5	1.906e-06	5.117e-08	1.177e-08	6.960e-07	7.008e-08	1.065e-06	1.168e-08	1.264e-10
7.6	1.833e-06	3.675e-08	1.064e-08	7.923e-07	4.890e-08	9.357e-07	8.491e-09	9.080e-11
7.7	1.800e-06	2.636e-08	9.610e-09	9.006e-07	3.417e-08	8.231e-07	6.152e-09	6.513e-11
7.8	1.803e-06	1.888e-08	8.664e-09	1.022e-06	2.391e-08	7.252e-07	4.444e-09	4.664e-11
7.9	1.840e-06	1.350e-08	7.802e-09	1.159e-06	1.676e-08	6.397e-07	3.201e-09	3.336e-11
8.0	1.913e-06	9.713e-09	7.065e-09	1.321e-06	1.167e-08	5.611e-07	2.323e-09	2.400e-11
8.1	2.034e-06	7.069e-09	6.473e-09	1.524e-06	8.039e-09	4.865e-07	1.714e-09	1.747e-11
8.2	2.195e-06	5.135e-09	5.920e-09	1.754e-06	5.547e-09	4.226e-07	1.260e-09	1.269e-11
8.3	2.397e-06	3.722e-09	5.402e-09	2.016e-06	3.835e-09	3.678e-07	9.228e-10	9.196e-12
8.4	2.643e-06	2.693e-09	4.920e-09	2.311e-06	2.657e-09	3.208e-07	6.735e-10	6.653e-12
8.5	2.934e-06	1.945e-09	4.473e-09	2.645e-06	1.844e-09	2.803e-07	4.900e-10	4.804e-12
8.6	3.274e-06	1.402e-09	4.059e-09	3.022e-06	1.282e-09	2.453e-07	3.555e-10	3.463e-12
8.7	3.668e-06	1.009e-09	3.679e-09	3.448e-06	8.926e-10	2.150e-07	2.572e-10	2.493e-12
8.8	4.122e-06	7.255e-10	3.330e-09	3.929e-06	6.222e-10	1.887e-07	1.858e-10	1.792e-12
8.9	4.643e-06	5.213e-10	3.012e-09	4.473e-06	4.341e-10	1.657e-07	1.340e-10	1.288e-12
9.0	5.241e-06	3.744e-10	2.723e-09	5.092e-06	3.029e-10	1.456e-07	9.650e-11	9.249e-13
9.1	5.927e-06	2.689e-10	2.462e-09	5.796e-06	2.114e-10	1.279e-07	6.949e-11	6.643e-13
9.2	6.718e-06	1.933e-10	2.228e-09	6.603e-06	1.474e-10	1.123e-07	5.004e-11	4.775e-13
9.3	7.631e-06	1.391e-10	2.018e-09	7.531e-06	1.026e-10	9.844e-08	3.607e-11	3.436e-13
9.4	8.692e-06	1.003e-10	1.832e-09	8.604e-06	7.136e-11	8.616e-08	2.604e-11	2.477e-13
9.5	9.191e-06	6.705e-11	1.542e-09	9.120e-06	4.581e-11	6.962e-08	1.743e-11	1.657e-13

Table 4.11 (Continued)

pH	CtCu (moles/liter)	Cu (moles/liter)	CuOH (moles/liter)	Cu(OH)2 (moles/liter)	CuHCO3 (moles/liter)	CuCO3 (moles/liter)	CuSO4 (moles/liter)	CuCl (moles/liter)
9.6	9.174e-06	4.231e-11	1.225e-09	9.120e-06	2.756e-11	5.273e-08	1.101e-11	1.045e-13
9.7	9.161e-06	2.669e-11	9.731e-10	9.120e-06	1.645e-11	3.963e-08	6.951e-12	6.595e-14
9.8	9.150e-06	1.684e-11	7.730e-10	9.120e-06	9.732e-12	2.951e-08	4.388e-12	4.161e-14
9.9	9.142e-06	1.063e-11	6.140e-10	9.120e-06	5.699e-12	2.176e-08	2.770e-12	2.626e-14
10.0	9.136e-06	6.705e-12	4.877e-10	9.120e-06	3.300e-12	1.586e-08	1.748e-12	1.657e-14
10.1	9.132e-06	4.231e-12	3.874e-10	9.120e-06	1.887e-12	1.142e-08	1.103e-12	1.045e-14
10.2	9.129e-06	2.669e-12	3.077e-10	9.120e-06	1.066e-12	8.119e-09	6.963e-13	6.595e-15
10.3	9.126e-06	1.684e-12	2.444e-10	9.120e-06	5.941e-13	5.698e-09	4.394e-13	4.161e-15
10.4	9.124e-06	1.063e-12	1.942e-10	9.120e-06	3.270e-13	3.948e-09	2.773e-13	2.626e-15
10.5	9.123e-06	6.705e-13	1.542e-10	9.120e-06	1.777e-13	2.702e-09	1.750e-13	1.657e-15
10.6	9.122e-06	4.231e-13	1.225e-10	9.120e-06	9.551e-14	1.828e-09	1.104e-13	1.045e-15
10.7	9.121e-06	2.669e-13	9.731e-11	9.120e-06	5.078e-14	1.223e-09	6.968e-14	6.595e-16
10.8	9.121e-06	1.684e-13	7.730e-11	9.120e-06	2.675e-14	8.111e-10	4.396e-14	4.161e-16
10.9	9.121e-06	1.063e-13	6.140e-11	9.120e-06	1.397e-14	5.333e-10	2.774e-14	2.626e-16
11.0	9.121e-06	6.705e-14	4.877e-11	9.120e-06	7.244e-15	3.482e-10	1.750e-14	1.657e-16

effluent pH values will result in even lower levels of bicarbonate. Levels of the carbonate ion increase with pH, though no irrigation limit for carbonate was found.

TDS

Equilibrium modeling with Minteq indicated that the blowdown water is oversaturated with respect to several constituents, including the following solids through the pH range 7-11: bixbyite (Mn_2O_3), diaspore ($Al_2O_3.2H_2O$), otavite ($CdCO_3$), fluorite (CaF_2), malachite ($Cu_2(OH)_2CO_3$), hematite Fe_2O_3, chrysotile ($Mg_3Si_2O_5$), magnesite ($MgCO_3$), fluorapatite ($Ca_5F(PO_4)_3$), lead hydroxide ($Pb(OH)_2$), diaspore ($Al_2O_3.2H_2O$), copper hydroxide ($Cu(OH)_2$), nickel hydroxide ($Ni(OH)_2$), brucite ($Mg(OH)_2$), $ZnSiO_3$ and tremolite ($Ca_2Mg_5Si_2O_{22}(OH)_2$). The solid phase which with the largest precipitating mass is calcium carbonate ($CaCO_3$). The projected effluent TDS was calculated by summation of the significant ions remaining in solution after equilibrium. Calcium, magnesium, sulfate, carbonate, chloride, sodium, potassium, nitrate and fluoride ions are the significant contributors to the mass of dissolved solids. The TOC in the blowdown water is expected to degrade and not contribute to effluent TDS. Values of TDS were calculated to decrease with increasing pH. Levels of TDS were calculated to vary from 955 mg/l at pH 7 to 598 mg/l at pH 9.

Summary

For the inorganic constituents of the blowdown water, only copper, cadmium, fluoride, bicarbonate and TDS are expected to exceed irrigation water quality standards directly from the cooling tower. The expected degree of treatment in a constructed wetlands was calculated from precipitation and complexation equilibrium. The level of TDS was calculated to be reduced, but even at blowdown concentrations would only require proper management for direct irrigation. Bicarbonate concentrations were calculated to be reduced by at least 50%, requiring only proper management for irrigation. The concentration of cadmium was calculated to be reduced well below the irrigation water quality standard for constructed wetlands effluent of pH 7 - 11. Copper was calculated to be reduced for constructed wetlands effluent from pH 7 - 9.2, which is expected under normal conditions. In addition, adsorption, which was not included in the equilibrium modeling, is the other predominant metal removal mechanism and should further reduce metal concentrations. Comparison of the equilibrium modeling with field results from Santee, as discussed later, possibly indicates that significant copper removal may occur by adsorption/ion exchange. Importantly, because cadmium and copper removal will occur to a sufficient degree by precipitation alone, the long-term metal removal capacity of the constructed wetlands should remain adequate. Fluoride was calculated to be reduced below pH 8, though the total fluoride levels will still exceed the limit, requiring reduction by mixing with stormwater or permission from the TDHE to exceed established irrigation limits. Excessive accumulations of metals in the crop soils was shown not to be a problem, even if irrigating with untreated blowdown water.

Based on the above, fluoride, then, is believed to be the controlling pollutant. No field data for the removal of fluoride in a constructed wetlands was discovered, and insufficient precipitation was noted in equilibrium modeling to reduce the fluoride concentration below the irrigation water quality standard. Fluoride and other monovalent species are very soluble. Therefore, planning on reducing fluoride concentrations below the irrigation water quality limit with a constructed wetlands alone is not warranted. However, fluoride concentrations in excess of irrigation limits may not present a serious environmental hazard. The irrigation water quality limits reported in the literature and by TDHE are only suggested limits, and increases may be allowed if proper monitoring is performed. Blowdown concentrations of fluoride should not cause toxic accumulations in crops (Tschantz, et al., 1990) By coordinating with the TDHE and instituting a careful monitoring plan, direct irrigation with the constructed wetlands effluent may be permissible.

Mixing with Saturn site stormwater runoff prior to irrigation will ensure fluoride concentrations are below irrigation limits. As discussed later, Saturn stormwater runoff is projected to be acceptable for direct spray irrigation without requiring treatment in the constructed wetlands. Utilization of stormwater runoff as a diluent will reduce fluoride (as well as other inorganic blowdown constituents) concentrations to acceptable levels for spray irrigation without treatment in a constructed wetlands. Utilization of stormwater runoff will also reduce Saturn's impact on the environment and improve crop yields.

If dilution with stormwater is utilized to reduce fluoride concentrations, a maximum total volume of 3:1 (ratio of volume of stormwater and blowdown water to the volume of blowdown water) would be required for reduction to the TDHE limit. The required volume of stormwater is based on the stormwater not containing a significant concentration of fluoride.

Of course, the same maximum volume ratio of total water to blowdown water requirements would result if a constructed wetlands was not utilized. However, use of constructed wetlands would reduce total pollutant loadings to the crops, and provide additional treatment for the organic chemicals contributed by the corrosion inhibitor and biocide, as discussed later.

Comparison of the Equilibrium Modeling Results to an Operating Constructed Wetlands

To test the validity of equilibrium modeling to predict effluent metal concentrations in a constructed wetlands, equilibrium modeling results were compared to results reported from an operating constructed wetlands. Equilibrium modeling was used to try to match results reported from the Santee, California constructed wetlands. The Santee wetlands is a SFS filled with gravel and has overflow rates similar to those recommended for Saturn. Copper, cadmium and zinc were added to the wetlands in a controlled manner to test the ability to remove metals as discussed in Chapter 2. Copper was reduced from 10.68 mg/l to 0.059 mg/l. Cadmium was reduced from 0.532 mg/l to below 0.004 mg/l. Zinc was reduced from 11.28 mg/l initially to 0.37 mg/l, but the effluent increased to 1.35 mg/l later in the study. The zinc amended bed was the only cell to show decreased metal removal capability during the approximately 18 month study.

There were some unknown elements in comparing equilibrium modeling results to the Santee constructed wetlands. For example, other wastewater constituents can exhibit a significant effect on metal solubility, as magnesium and sulfate concentrations influence the projected Saturn constructed wetlands effluent. Other constituents were not reported, though the Santee wetlands was also treating municipal wastewater. The pH was listed as a general range only. In addition, the bed media was reported as gravel, though not specifically identified as limestone gravel which was used in the equilibrium modeling calculations. Carbonate ions were, however, listed as one of the precipitating ions. However, as discussed later, the equilibrium modeling results corresponded well with the results from Santee, indicating the potential to predict metal removal in a constructed wetlands. Subsequent inclusion of more detailed information from an operating constructed wetlands would allow further refinement.

Equilibrium modeling was conducted with no ionic strength or other components, and a solubility range was generated from pH 7 to 9. The total metal solubility at the entire pH range was checked, though metals solubility varies markedly with pH. In addition, zinc was included, although not a component of concern in the Saturn blowdown water, because of the increase in effluent zinc concentration later in the study.

Copper

In comparing equilibrium modeling predicted values of effluent metal concentration with values reported from Santee, copper yielded less correlation with than either cadmium or zinc, though an interesting observation was noted. Equilibrium modeling calculated copper effluent concentrations increasing from 0.12 mg/l to 0.58 mg/l over the pH range 7 - 9., compared to the Santee effluent of 0.059 mg/l. Since the equilibrium modeling predicted concentrations were above the Santee effluent, adsorption/ion exchange may play a role in the removal of copper from a constructed wetlands, though other factors may also be responsible for the additional removal. However, if the additional removal were attributed entirely to adsorption/ion exchange, metal concentrations would be reduced from precipitation only values by approximately 0.06 mg/l to 0.52 mg/l, or at most 5% of the total removal. Table 4.12 shows the equilibrium modeling results versus values reported from Santee for copper, cadmium and zinc.

Cadmium

Equilibrium modeling calculated effluent cadmium concentrations which decreased from 0.003 mg/l at pH 7 to 0.001 mg/l at pH 9 compared to the effluent reported at Santee of below 0.004 mg/l, providing excellent agreement with calculated equilibrium values. Adsorption/ion exchange possibly plays a less significant role in the removal of cadmium from a SFS constructed wetlands, though other factors could also influence the observed concentrations.

Zinc

Zinc was used for comparison of equilibrium modeling results to Santee, though not a concern in the Saturn blowdown, because of the phenomenon noted at Santee of the zinc effluent concentrations rising from an initial value of 0.37 mg/l to 1.35 mg/l. If adsorption/ion exchange is an important factor in removing metals from a constructed wetlands, the capacity will be finite due to exhaustion of exchange sites. If the Santee effluent zinc concentrations rose after time from a value below what is predicted from precipitation alone to a value close to the equilibrium value with the solid phase, the contribution of adsorption/ion exchange to metal removal may be illuminated.

The calculated effluent concentrations of zinc ranged from 4.91 mg/l at pH 7 to 0.37 mg/l at pH 9. Zinc carbonate is the stable solid phase below pH 8.2 and zinc hydroxide is the stable phase at higher pH values. Zinc oxide was not allowed to precipitate for the same reasons copper oxide was not allowed to precipitate as discussed in Chapter 3. At pH 8.2, the effluent zinc concentration was calculated as 1.52 mg/l which is comparable to the subsequent Santee zinc effluent of 1.35 mg/l. One possible explanation is, as discussed, the initial effluent Santee zinc value resulted from the contribution of adsorption/ion exchange to zinc removal, while the

Table 4.12 Calculated Effluent Concentration Versus Results from the Santee Constructed Wetlands

Metal	Santee Effluent Concentration (mg/l)	Predicted Effluent Concentration from Equilibrium Modeling[a] (mg/l)
Copper	0.059	0.12 - 0.58
Cadmium	< 0.004	0.003 - 0.001
Zinc	0.37 - 1.35[b]	4.91 - 0.37

a. Effluent concentration range is for pH 7 - 9.

b. Effluent zinc concentration increased from an intial value of 0.37 mg/l to 1.35 mg/l later in the study.

subsequent increase in the effluent zinc concentration was due to the exhaustion of exchange sites. However, an alternate explanation is a shift in effluent pH. At pH 9 equilibrium modeling calculated the expected zinc effluent concentration as 0.37 mg/l which is exactly the initial Santee effluent zinc concentration. Therefore a decrease in effluent pH from 9 to approximately 8.2 rather than the exhaustion of exchange sites may be responsible for the change. The change in effluent pH could be caused by a number of factors such as change in influent wastewater (the Santee constructed wetlands was also treating municipal wastewater) or a decrease in biological activity caused by a season change.

Summary

Equilibrium modeling calculated effluent copper concentrations above values reported for the Santee wetlands, possibly indicating the contribution of the adsorption/ion exchange mechanism to copper removal, although other factors could have contributed to the additional removal as well. Calculated effluent concentrations for cadmium and zinc were in the same range as the values reported from Santee. The increase in zinc effluent in time could have occurred as a result of a change in effluent pH as well as the exhaustion of adsorption/ion exchange sites. Comparison of the calculated values to the results reported from Santee demonstrated that equilibrium modeling can potentially predict maximum effluent metal concentrations, with additional removal expected, possibly from adsorption/ion exchange.

Fate of the Organic Blowdown Water Constituents in the System

The impact of the organic compounds contributed by the corrosion inhibitor and biocide on the system was determined first by a review of pertinent previous work which has been reported in the literature as discussed in Chapter 2. The following is a summary of the findings and conclusions and recommendations from the literature review.

The biocide contains copper nitrate trihydrate and two isothiazoline biocides. The copper could be reduced by precipitation in the constructed wetlands. The isothiazoline biocides would not be environmentally persistent,degrading by a variety of mechanisms, including chemical, biological and photoxidative degradation. Wetlands plants would readily absorb and metabolize these compounds. The biocide will, however, be used in high concentrations, approximately 250 mg/l for shock treatment. The isothiazoline biocides are significantly more toxic than the compounds contributed by the corrosion inhibitor , and would be toxic to microorganisms and fish until degraded. The copper in the biocide will also use adsorption/ion exchange sites in the constructed wetlands. Therefore, the blowdown effluent should be not directed to the constructed wetlands and wastewater irrigation system during shock treatment with the biocide to minimize potential environmental impacts.

The corrosion inhibitor contains two phosphonates, a tolytriazole and an acrylic acid polymer which may impact the system. Both phosphonates adsorbed significantly on sewage sludge. One of the phosphonates, HEDP, should be readily removed in a constructed wetlands by adsorption, photodegradation, and will not bioconcentrate in aquatic life. The other phosphonate, PBTC, will not biodegrade. However, the toxicity of PBTC indicates blowdown concentrations will not be hazardous.

The acrylic acid polymer will not biodegrade, but would require concentrations significantly higher than the projected blowdown concentration to be toxic. The tolytriazole is significantly more toxic than the other organic constituents of the blowdown water and will not degrade. However, no harmful environmental effects have been reported for concentrations as low as would be expected in the blowdown water. Careful monitoring would be required to determine the fate of all the blowdown constituents in the system.

Octanol/Water Partition Coefficients

For those compounds which have little documented information on environmental fate, Paige and Chang (1985) have presented a method to predict their behavior in soils by an estimated or measured value of the octanol/water partition coefficient. Because organics in wastewater irrigation can be toxic or carcinogenic, immobilization of an organic compound in the soil media would prevent the compound from entering the soil water for uptake by the crops.

K_{ow} is the ratio of the concentration of a chemical in the octanol phase to the concentration in an aqueous phase in equilibrium. K_{ow} is a measure of the tendency of a chemical to concentrate in a aqueous phase or an organic phase (organic matter in soil or plants and animals). At the extremes, chemicals with K_{ow} less than 10 will be water soluble and have little tendency to accumulate in soils or aquatic life, while chemicals with K_{ow} greater than 10,000 will exhibit the opposite behavior (Lyman, et al., 1982). K_{ow} can be measured experimentally, calculated from the chemical's structure, or calculated by regression equations from water solubility or partition coefficients measured in other solvent/water systems.

The method is based on modeling soil adsorption on a linear adsorption isotherm, which is valid for low concentrations of solute. The linear isotherm is described by the equation

$$\frac{X}{M} = KC \qquad (4\text{-}1)$$

where x = amount of solute adsorbed (micrograms/ml),

M = mass of soil (g) ,

K = soil adsorption constant (ml/g),

C = equilibrium solute concentration (micrograms/ml).

K is a function of both the compound involved and the soil type. The isotherm can be rewritten in terms of the fraction of organic matter in the soil

$$\frac{x}{M_{oc}} = \frac{KC}{F_{oc}} = K_{oc}C \qquad (4\text{-}2)$$

where M_{oc} = mass of soil organic content (g),

F_{oc} = fraction of organic matter in the soil,

K_{oc} = soil adsorption constant of organic matter (ml/g).

The advantage of expressing the adsorption coefficient in terms of K_{oc} is that K_{oc} is a function only of the compound in consideration, but is not a function of the soil type.

K_{oc} is related to the octanol/water partition coefficient, K_{ow} by any of the following empirical equations presented in the literature (Paige and Chang, 1985):

$$K_{oc} = 0.63\ K_{ow} \qquad (4\text{-}3)$$

$$K_{oc} = 0.72\ \log K_{ow} + 0.49 \qquad (4\text{-}4)$$

$$K_{oc} = 0.544\ \log K_{ow} + 1.377 \qquad (4\text{-}5)$$

The value of the octanol/water partition coefficient can be calculated from the chemical's water solubility by the following equation for a broad range of organic compounds (Lyman, et al., 1982)

$$\log S = -1.37 \log K_{ow} + 7.26 \qquad (4\text{-}6)$$

where S = solubility (micromoles/liter).

The solubility of tolytriazole in water was measured as 0.05 % by weight at 25^{o}C (Korpics, 1974). From the solubility and equation 4-6, the log octanol/water partition coefficient for the tolytriazole was calculated as 2.69. Applying equations 4-3 through 4-5, the resulting K_{oc} values ranged from 267 - 692. Compounds with values of K_{oc} greater than 200 - 300 are expected to be effectively immobilized in the soil during wastewater irrigation (Paige and Chang, 1985).

Values of water solubility for the other organic constituents of the corrosion inhibitor were not found. Leo and Hansch (1979) have developed a fragment method for estimating K_{ow} from a chemical's structure. The chemical is broken down into individual chemical fragments which have assigned values, and summing the values for the individual fragments and corrections for bond factors yields the log K_{ow}. This method has calculated log K_{ow} within 0.2 units of experimentally measured values for many chemicals.

The calculation of K_{ow} for polymers such as the acrylic acid compound was not addressed specifically by Leo and Hansch or Lyman and to this author there seems to be an inherit problem in applying this method to polymers. The calculation of K_{ow} by this method is based on assigning quantitative values for fragments of molecules, based on the fragments relative affinity for an aqueous phase or an organic phase. To this author, the relative affinity of a polymer for an aqueous phase or an organic phase could not be determined by summing individual fragments. For example, a polymer with a chain length of 1000 monomers would have a calculated K_{ow} approximately (corrections for the additional bonds would lower the sum somewhat) 100 times a polymer of chain length of 10 monomers. Since the relative affinity of the polymer is determined by the chemistry of the two molecules, which would likely be fairly similar, the approach seems to have a fundamental problem for polymers. Due to the preceding rationale, and the fact that the actual chemical structure for the polymer was not given by the Chemical Abstracts Data Base precluded calculation of the log K_{ow} for the polymer.

The values of K_{ow} for the two phosphonates could not be calculated by the fragment constant method because the value for the phosphono fragment in a chain was not given. In any case, the K_{ow} for the phosphonate HEDP was less than 0.001, though the compound still exhibited significant adsorption (Steber and Wierich, 1986).

Summary

The blowdown water should not be directed to the system during shock use of the biocide. The organics contributed by the corrosion inhibitor are not expected to exhibit adverse environmental impacts (other than persistence)because of one or more of the following reasons for each compound: low toxicity at the expected blowdown concentration, low bioaccumulation potential, or effective removal in a constructed wetlands or crop soils by adsorption or degradation. However, careful monitoring of the corrosion inhibitor fate and effect should be performed. If the organic constituents are not removed in the constructed wetlands, crop irrigation system, substitution of components in the corrosion inhibitor is recommended to alleviate any concerns.

Fate of the Stormwater in the System

Although stormwater runoff can have a deleterious effect on the environment as discussed in Chapter 2, the irrigation water quality standards are significantly higher than the projected stormwater quality as shown in Table 4.13 for the primary pollutants reported in NURP. As a result, Saturn stormwater runoff generally could be used directly for crop irrigation without the need for treatment in a constructed wetlands.

Table 4.13 Comparison of Primary Pollutants in Stormwater Runoff with Irrigation Water Quality Standards

Pollutant	Concentration (mg/l)	Irrigation Limit (mg/l)[a]	TDHE Limit (mg/l)[b]
Nitrogen-N	2.18	5	
Copper	0.034	0.2	0.4
Lead	0.144	5	10
Zinc	0.160	2	4

a. Irrigation Limit from Wescot, D. W. and R. S. Ayers. "Irrigation Water Quality Criteria" In: Irrigation with Reclaimed Municipal Wastewater, Lewis Publishers, Chelsea, MI. 1985.

b. TDHE Limit from Tennessee Department of Health and Environment, Chapter 16, Slow Rate Land Treatment in Design Criteria of Sewage Treatment Works.

Conceptual Design of the Constructed Wetlands

The type of constructed wetlands recommended for Saturn is a Subsurface Flow System (SFS). However, a small portion of the wetlands should be devoted to a Free Water Surface System (FWS) as discussed below. An SFS is a shallow, typically 2 to 3 feet deep, wetlands with a porous media, either gravel, soil or sand, to support emergent plant growth. Actual water flow remains below the surface so there is no free standing water.

An SFS is recommended for Saturn primarily because of the metal concentrations in the blowdown water. Adsorption/ion exchange is an important removal mechanism for metals, as well as other pollutants, and is facilitated in an SFS because of the high surface area per unit volume of wetlands, although adsorption/ion exchange is not required to to reduce the levels of copper or cadmium in the blowdown water. Although an SFS is initially more expensive than a free water surface system (FWS), the other predominant type of wetland, because of the bed media cost, an SFS may be operated at a higher loading rate and thus require less land area for a given wastewater flow. SFS also exhibits less problems with mosquitos.

The bed media should be a limestone gravel. Limestone gravel is not required to provide carbonate species for metal carbonate precipitation because the blowdown water is oversaturated with calcium carbonate directly from the tower. However, limestone gravel is ubiquitous and relatively inexpensive in Tennessee. Use of limestone gravel would also ensure metal precipitation if carbonate species levels in the blowdown water are lower than the projected values used in this investigation. As discussed earlier, a constructed wetlands may not be necessary at all. However, a constructed wetlands will act as a buffer for the system and provide degradation opportunities for the organic compounds.

Although loading rates for constructed wetlands reported in the literature are widely variable, approximately 10 acres is required for treating blowdown water at the summer average rate of approximately 500,000 gallons per day, based on a cooling tower operating with three cycles. If the cooling tower is operated with five cycles, the average summer blowdown rate will be approximately 250,000 gallons per day, and the resulting wetland size would be 5 acres.The required loading rate was determined from the Santee constructed wetlands which demonstrated copper and cadmium removal in an SFS (Gersberg, et al., 1984). Sizing the wetlands for the peak summer blowdown rate is not necessary because the loading rate is not rigorously derived in the literature sources, and a higher loading rate may work as effectively. In addition, the supplemental storm water/make-up water should reduce pollutants below irrigation limits if increasing effluent concentrations are encountered during peak blowdown periods. During off-peak periods, the remaining wetlands area may be used to treat stormwater runoff or other Saturn wastewaters.

The length to width (L/W) ratio of an SWS should be as high as possible without causing above surface flooding, and several wetlands have found that L/W ratios > 1/1 have caused flooding. The L/W ratio of an FWS should be large, approximately 10/1, to maintain plug flow conditions. The total recommended land area for the wetland is 10 acres (or 5 acres) as discussed earlier. However, the wetland should be divided into separate cells which are independently drainable. Periodic draining may be required for maintenance and this also enhances mosquito control. The wetlands should be divided into two parallel units of three cells in series for a total of six cells. The parallel cells will allow two independent treatment units for maintenance. The first two cells in series (four cells total for the two units) should be SFS cells. The final cell in series (two cells total for the two units) should be an FWS cell. Approximately 80% of the total land area should be devoted to SFS. The FWS cells are recommended to compare the performance of the two types of wetlands in treating Saturn wastewaters and stormwater and to enhance photodegradation of the organic components in the corrosion inhibitor. The constructed wetlands should have an impermeable liner, either synthetic or natural, to prevent ground water contamination. The slope of the bed should be approximately 1%. The nominal design parameters recommended for the Saturn constructed wetlands are shown in Table 4.14.

The costs for constructed wetlands reported in the literature are also widely variable but $20,000 per acre seems to be a fairly typical value, though higher values have been reported. Costs per acre must be a function of wetlands size (smaller wetlands should be more expensive than large wetlands on a per acre basis) though no discernable trend was noticed in the literature. TVA reported extremely wide variances in cost per acre for constructed wetlands for treating mine and ash pond drainage, but felt $40,000 per wetland was a typical value. Wetlands cost may also be variable from site to site because of the difference in land, equipment and labor costs. Almost all of the cost of a constructed wetlands is encumbered in the initial construction. Maintenance costs are typically only a few thousand dollars per year.

Table 4.14 Recommended Nominal Design Parameters for the Saturn Constructed Wetlands

Total Wetlands Area	
Five Cycles	5 Acres
Three Cycles	10 Acres
Number of Cells	Minimum of 6 (4 SWS, 2 FWS)
Depth	3 Feet
Slope of Bed	1%
Liner	Natural or synthetic to prevent ground water contamination
Estimated Capital Cost	$ 20,000 per acre[a]
Annual Maintenance Cost	$ 1,000

a. Saturn performed a detailed cost estimate resulting in a projected cost of $139,000 per acre.

Chapter 5

CONCLUSIONS

The major conclusion of the investigation is that a constructed wetlands, spray irrigation system has the potential to safely and successfully treat the cooling tower blowdown water, if supplemented with site stormwater runoff to reduce fluoride concentrations below irrigation limits. The blowdown water quality is acceptable for direct spray irrigation of crops except for levels of bicarbonate, TDS, cadmium, copper and fluoride. The constructed wetlands would effectively remove cadmium and copper from the blowdown water, reduce management problems with bicarbonate and TDS, reduce overall pollutant loadings to the crops, and provide adsorption and biodegradation opportunity for the organics in the corrosion inhibitor. However, because removal of fluoride in a constructed wetlands to below irrigation water quality standards is not expected, treatment in a constructed wetlands may not reduce supplemental stormwater or make-up water requirements (i.e. the same volume of stormwater or makeup water may be required whether or not a constructed wetlands is utilized). The long-term capacity of the constructed wetlands to remove cadmium and copper is also adequate to treat the blowdown water to irrigation water quality standards. Utilization of blowdown water would conserve sewer capacity, eliminate wastewater disposal charges, and improve crop yields. The stormwater required as a supplement would increase crop yields, and reduce the impact of stormwater runoff on the environment.

Specific Conclusions

1. Based on a comparison of the projected blowdown water inorganic constituent concentrations with irrigation water quality standards established by the TDHE, direct irrigation with blowdown water is permissible except for concentrations of copper, cadmium, TDS, bicarbonate and fluoride. From equilibrium modeling calculations bicarbonate concentrations will

be reduced by at least 50% to a level requiring only proper management controls. TDS will be reduced in the constructed wetlands, but only requires proper management controls even at blowdown concentrations. Equilibrium modeling calculations indicate copper and cadmium will be effectively removed in a constructed wetlands at the expected effluent pH range of 7 - 8.5. Fluoride removal to below irrigation water quality standards is not likely. Therefore, blowdown water treated in a constructed wetlands will require at a maximum supplemental storm water make-up by approximately 3:1 (3 parts combined volume of blowdown water and stormwater to 1 part blowdown water). Fluoride concentrations would need to be monitored in soils and crops.

2. Calculated values of constructed wetlands effluent metal concentrations matched the data reported from the Santee, California constructed wetlands, establishing the potential to mathematically describe metal removal in a constructed wetlands. The Santee wetlands exhibited lower effluent copper concentrations than calculated from equilibrium modeling, possibly indicating copper removal by adsorption/ion exchange. The effluent cadmium concentrations reported at Santee agreed well with equilibrium values. The decrease in zinc removal over time could be attributed to either the exhaustion of adsorption/ion exchange sites or a change in the effluent pH.

3. Based on information provided by the manufacturer and reported in the literature, and calculations of the octanol/water partition coefficient, the organics contributed by the corrosion inhibitor exhibit one or more the following for each compound: low toxicity at expected blowdown concentrations, low bioaccumulation potential, or effective removal in a constructed wetlands or crop soils by adsorption or degradation. Some of the compounds, however, may not degrade and will be environmentally persistent. Careful monitoring in the constructed wetlands, crops, and crop soils is required. If the organic constituents are not removed in the constructed wetlands, crop irrigation system, substitution of components in the corrosion inhibitor is recommended to alleviate any concerns.

4. Based on information in the literature review, the organics contributed by the biocide will degrade satisfactorily by a variety of mechanisms. However, the biocide will be used in high shock concentrations, and these compounds are significantly more toxic than those contributed by the corrosion inhibitor. Therefore, the blowdown water should not be directed to the constructed wetlands/crop irrigation system during periods when the biocide is used.

5. Calculations of the potential buildup of metals in the crop soils indicated that irrigation with untreated blowdown water could occur for 19 years before exceeding TDHE guidelines. Irrigation with untreated blowdown water could, however, increase background metal concentrations in the soil.

6. The recommended constructed wetlands size to treat the blowdown water is 10 acres for the three cycle cooling tower operation and 5 acres for the five cycle tower operation. The estimated construction cost is \$200,000 and \$100,000 respectively. The wetlands should be approximately 80% SFS with the remainder FWS. A minimum of 6 independently drainable cells, 4 SFS and 2 FWS are recommended.

7. Direct crop irrigation with the blowdown water may be possible by establishing a monitoring program acceptable to the state to allow irrigation with water that does not meet irrigation water quality limits, eliminating the need for the constructed wetlands. However, a constructed wetlands would reduce total pollutant loads to the crops, and act as a buffer for the system.

8. Stormwater quality meets irrigation water quality criteria, and would not require treatment in the constructed wetlands.

9. Operating the cooling tower in the five cycle mode will result in higher pollutant concentrations in the blowdown water, but will reduce land requirements for a constructed wetlands by fifty percent.

Recommendations for Further Study

1. Construction of a pilot scale or laboratory scale, constructed wetlands is recommended prior to implementation at Saturn because of the following advantages:

a. Determination of the optimum hydraulic loading rate effective in treating the Saturn blowdown water could reduce land area requirements for the constructed wetlands.

b. The efficiency of the wetlands to treat pollutants of interest such as fluoride, the corrosion inhibitor, etc. could be determined. This could have impacts in the system design. If, for example, fluoride were removed, stormwater dilution would not be required. If the corrosion inhibitor compounds were not removed in the constructed wetlands, crop irrigation system, another corrosion inhibitor could be identified.

c. Pollutant removal effectiveness documented in the literature could be verified.

d. Equilibrium modeling results could be compared to the pilot scale or laboratory scale wetlands performance.

2. As documented in this investigation, a further mathematical description of the degree of metal removal in a constructed wetlands is warranted. Further study would allow determination of adsorption isotherm data, allowing inclusion in equilibrium modeling.

3. Measurement of actual blowdown water quality and stormwater quality (rather than projected values) would allow a more accurate prediction of environmental fate and effect.

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APPENDICES

APPENDIX 1

```
! ***************************************************************************************************
! *                                                                                                 *
! * Program to calculate copper and cadmium concentrations in equilibrium with calcium              *
! * carbonate.                                                                                      *
! *                                                                                                 *
! *Program written in True Basic on the Macintosh II                                                *
! *                                                                                                 *
! *Written by Mark Barnett for a thesis in partial fulfillment for the requirements of the degree   *
! *M. S. in Environmental Engineering, August 1991                                                  *
! *                                                                                                 *
! *                                                                                                 *
! *                                                                                                 *
! *                                                                                                 *
! *                                                                                                 *
! ***************************************************************************************************

! Input values are entered and read from the subroutine Input

CALL INPUT

! Equilibrium constants not associated with the metal of interest are read from the subroutine
! Equilibrate CaCO3

CALL EQUILIBRATE_CACO3

! Define equilibrium ratios for the possible solid combinations

DEF QMOH2 = M * OH^2
DEF QM2OH2CO3 = M^2 * OH^2 * CO3
DEF QMCO3 = M * CO3

DEF RATIO_MCO3 = QMCO3/KsoMCO3
DEF RATIO_MOH2 = QMOH2/KsoMOH2
DEF RATIO_M2OH2CO3 = QM2OH2CO3/KsoM2OH2CO3

! Read metal specific equilibrium constants

IF UCASE$(Metal$) = "COPPER" THEN CALL COPPER

IF UCASE$(Metal$) = "CADMIUM" THEN CALL CADMIUM

! Correct equilibrium constants for ionic strength in the subroutine Activity Coefficients

CALL ACTIVITY_COEFFICIENTS

! Select effluent pH values to generate a pH - metal solubility curve

FOR pH = START_pH TO END_pH STEP INTERVAL_pH

    LET h = 10^(-pH)
    LET h = h/GAMMA_1
    LET OH = Kw/h

! Print intermediate iterative values if debug output option selected

IF OUTPUT_TYPE = 1 THEN
```

```
    PRINT USING "RATIO_MCO3=#.###^^^^" :RATIO_MCO3
    PRINT USING "RATIO_MOH2 =#.###^^^^" :RATIO_MOH2
    PRINT USING "RATIO_M2OH2CO3=#.###^^^^" :RATIO_M2OH2CO3
    PRINT

END IF

! Attempt to equilibrate the solid metal carbonate in the subroutine Precipitate MCO3

CALL PRECIPITATE_MCO3

! Check if the solution is oversaturated with the metal carbonate hydroxide

IF RATIO_M2OH2CO3 > 1 OR SOLID$ = "SOLUTION UNDERSATURATED" THEN

! Attempt to equilibrate the solid metal hydroxide carbonate in the subroutine
! Precipitate M2(OH)2CO3

    CALL PRECIPITATE_M2OH2CO3

END IF

! Check if the solution is oversaturated with the metal hydroxide

IF RATIO_MOH2 > 1 OR SOLID$ = "SOLUTION UNDERSATURATED" THEN

! Attempt to equilibrate the solid metal hydroxide  in the subroutine  Precipitate M(OH)2

    CALL PRECIPITATE_MOH2

END IF

! Call the subroutine Check to check ensure accuracy of final solution

CALL CHECK

! Call the subroutine output to print the specification output

CALL OUTPUT

NEXT pH

! End of main program - begin subroutines

! Calculate Species in Equilibrium with M(OH)2

SUB PRECIPITATE_MOH2

! Initialize values

    LET SOLID$ = "SOLID METAL HYDROXIDE PRECIPITATES"
    LET OLDIFFUNCTION = 0
    LET STEP = 0
    LET ITERATION = 0
    LET CtCO3 = 0
    LET CtCa = 0
```

```
! First loop to find the log range of the new solubility of CaCO3

    FOR N = -10 TO 1 STEP 1

! Supply a value for the calcium ion concentration

        LET Ca = 10^(N)

! Calculate equilibrium values of other species from the supplied calcium ion
! in the subroutine Calculate Values

        CALL  CALCULATE_VALUES

! Print intermediate iterative values if debug output option selected

         IF OUTPUT_TYPE = 1 THEN

            PRINT USING "S=#.###^^^^" :S
            PRINT

        END IF

! Define the difference function to test for convergence

        LET DIFFUNCTION = Ct0CO3 + S + MgCO3PRECIP - CtCO3

! Check to see if the difference function changed sign indicating the correct calcium ion
! concentration was passed

        IF DIFFUNCTION * OLDIFFUNCTION < 0 THEN

            LET TOTAL_SOL = Ca/10
            LET N = TOTAL_SOL
            LET OLDIFFUNCTION = 0
            EXIT FOR

        END IF

! Print intermediate iterative values if debug output option selected

        IF OUTPUT_TYPE = 1 THEN

            PRINT " ITERATION= "; SOLUTION =   ";Ca ; "    DIFFUNCTION = ";DIFFUNCTION

        END IF

        LET OLDIFFUNCTION = DIFFUNCTION

! Exit the loop if no solution passed

        IF N = 1 THEN

            LET SOLID$ = "Failed to Converge"
            EXIT SUB

        END IF
```

```
    NEXT N

! Final loop to solve for the actual new solubility of CaCO3

! Initialize values

    LET OLDIFFUNCTION = 0

    DO

! Count iterations and check against maximum allowable

        LET ITERATION = ITERATION + 1

        IF ITERATION > MAX_ITERATIONS THEN

            LET SOLID$ = "Iterations greater than maximum"
            EXIT DO

        END IF

! Supply a value for the calcium ion concentration

        LET Ca = TOTAL_SOL + N * STEP

! Calculate equilibrium values of other species from the supplied calcium ion
! in the subroutine Calculate Values

        CALL  CALCULATE_VALUES

! Define the difference function to test for convergence

        LET DIFFUNCTION = Ct0CO3 + S + MgCO3PRECIP - CtCO3

! Print intermediate iterative values if debug output option selected

        IF  OUTPUT_TYPE = 1 THEN

            PRINT "ITERATION =";ITERATION;"Ca= ";Ca;"DIFFUNCTION =";DIFFUNCTION
            PRINT

      END IF

! Check for convergence by comparing difference function to error criteria

        IF ABS(DIFFUNCTION)/CtCO3 < ERROR_CRITERIA THEN EXIT DO

! If the solution is passed, revise estimate of calcium ion concentration

        IF DIFFUNCTION * OLDIFFUNCTION < 0 THEN

            LET TOTAL_SOL = TOTAL_SOL + N*(STEP-1)
            LET N = N/10
            LET STEP = -1
            LET DIFFUNCTION =0
```

```
        END IF

        LET OLDIFFUNCTION = DIFFUNCTION
        LET STEP = STEP + 1

    LOOP

! Calculate equilibrium values fro other species after convergence

    LET M = KsoMOH2 / OH^2
    LET MOH = M * OH * BMOH
    LET MOH2aq = M * OH^2 * BMOH2
    LET MHCO3 = M * HCO3 * BMHCO3
    LET MCO3aq = M * CO3 * BMCO3
    LET MSO4aq = M * SO4 * BMSO4
    LET MCl = M * Cl * BMCl
    LET CtM = M + MOH + MOH2aq + MHCO3 + MCO3aq + MSO4aq + MCl
    LET CtSO4 = SO4 + CaSO4aq + MgSO4aq
    LET P = CtM - Ct0M
    IF P > 0 THEN LET SOLID$ = "SOLUTION UNDERSATURATED"
    LET I = 1


END SUB

SUB PRECIPITATE_MCO3

! Initialize values

    LET SOLID$ = "SOLID METAL CARBONATE PRECIPITATES"
    LET OLDIFFUNCTION = 0
    LET STEP = 0
    LET ITERATION = 0
    LET CtCO3 = 0
    LET CtCa = 0

! First loop to find the log range of the new solubility of CaCO3

    FOR N = -10 TO 1 STEP 1

! Supply a value for the calcium ion concentration

        LET Ca = 10^(N)

! Calculate equilibrium values of other species from the supplied calcium ion
! in the subroutine Calculate Values

        CALL  CALCULATE_VALUES

! Calculate M from mass balance equation

        LET P = CtCO3 - S - Ct0CO3 - MgCO3PRECIP
        LET CtM = Ct0M + P
        LET M = CtM/
(1+BMOH*OH+BMOH2*OH^2+BMHCO3*HCO3+BMCO3*CO3+BMSO4*SO4+BMCl*Cl)

! Print intermediate iterative values if debug output option selected
```

```
        IF OUTPUT_TYPE = 1 THEN

           PRINT USING "CtM=#.###^^^^" :CtM
           PRINT USING "M=#.###^^^^" :M
           PRINT USING "CO3=#.###^^^^" :co3
           PRINT USING "M * CO3 =#.###^^^^" :m*co3
           PRINT

        END IF

! Define the difference function to test for convergence

        LET DIFFUNCTION = M * CO3 - KsoMCO3

! Check to see if the difference function changed sign indicating the correct calcium ion
! concentration was passed

        IF DIFFUNCTION * OLDIFFUNCTION < 0 THEN

           LET TOTAL_SOL = Ca/10
           LET N = TOTAL_SOL
           LET OLDIFFUNCTION = 0
           EXIT FOR

        END IF

! Print intermediate iterative values if debug output option selected

        IF OUTPUT_TYPE = 1 THEN

           PRINT ITERATION; " SOLUTION =   ";Ca ; "    DIFFUNCTION = ";DIFFUNCTION

        END IF

        LET OLDIFFUNCTION = DIFFUNCTION

! Exit the loop if no solution passed

        IF N = 1 THEN

           LET SOLID$ = "Failed to Converge"
           EXIT SUB

        END IF

     NEXT N

! Final loop to solve for the actual new solubility of CaCO3

! Initialize values

     LET OLDIFFUNCTION = 0

     DO

! Count iterations and check against maximum allowable
```

```
        LET ITERATION = ITERATION + 1

        IF ITERATION > MAX_ITERATIONS THEN

            LET SOLID$ = "Iterations greater than maximum"
            EXIT DO

        END IF

! Supply a value for the calcium ion concentration

        LET Ca = TOTAL_SOL + N * STEP

! Calculate equilibrium values of other species from the supplied calcium ion
! in the subroutine Calculate Values

        CALL  CALCULATE_VALUES

! Calculate M from mass balance equation

        LET P = CtCO3 - S - Ct0CO3 - MgCO3PRECIP
        LET CtM = Ct0M + P
        LET M = CtM/
(1+BMOH*OH+BMOH2*OH^2+BMHCO3*HCO3+BMCO3*CO3+BMSO4*SO4+BMCl*Cl)

! Define the difference function to test for convergence

        LET DIFFUNCTION = M * CO3 - KsoMCO3

! Print intermediate iterative values if debug output option selected

        IF  OUTPUT_TYPE = 1 THEN

            PRINT  "ITERATION =";ITERATION;"Ca= ";Ca;"DIFFUNCTION =";DIFFUNCTION
            PRINT

        END IF

! Check for convergence by comparing difference function to error criteria

        IF ABS(DIFFUNCTION)/KsoMCO3 < ERROR_CRITERIA THEN EXIT DO

! If the solution is passed, revise estimate of calcium ion concentration

        IF DIFFUNCTION * OLDIFFUNCTION < 0 THEN

            LET TOTAL_SOL = TOTAL_SOL + N*(STEP-1)
            LET N = N/10
            LET STEP = -1
            LET DIFFUNCTION =0

        END IF

        LET OLDIFFUNCTION = DIFFUNCTION
        LET STEP = STEP + 1
```

```
    LOOP

! Calculate equilibrium values from other species after convergence

    LET MOH = M * OH * BMOH
    LET MOH2aq = M * OH^2 * BMOH2
    LET MHCO3 = M * HCO3 * BMHCO3
    LET MCO3aq = M * CO3 * BMCO3
    LET MSO4aq = M * SO4 * BMSO4
    LET MCl = M * Cl * BMCl
    LET CtSO4 = SO4 + CaSO4aq + MgSO4aq
    IF P > 0 THEN LET SOLID$ = "SOLUTION UNDERSATURATED"
    LET I = 1

END SUB

SUB PRECIPITATE_M2OH2CO3

! Initialize values

    LET SOLID$ = "SOLID METAL HYDROXIDE/CARBONATE PRECIPITATES"
    LET OLDIFFUNCTION = 0
    LET STEP = 0
    LET CtCO3 = 0
    LET ITERATION = 0
    LET CtCa = 0

! First loop to find the log range of the new solubility of CaCO3

    FOR N = -10 TO 1 STEP 1

! Supply a value for the calcium ion concentration

        LET Ca = 10^(N)

! Calculate equilibrium values of other species from the supplied calcium ion
! in the subroutine Calculate Values

        CALL  CALCULATE_VALUES

! Calculate M from mass balance equation

        LET P = CtCO3 - S - Ct0CO3 - MgCO3PRECIP
        LET CtM = Ct0M + 2 * P
        LET M = CtM/
(1+BMOH*OH+BMOH2*OH^2+BMHCO3*HCO3+BMCO3*CO3+BMSO4*SO4+BMCl*Cl)

! Print intermediate iterative values if debug output option selected

        IF OUTPUT_TYPE = 1 THEN

            PRINT USING "CtM=#.###^^^^" :CtM
            PRINT USING "M=#.###^^^^" :M
            PRINT USING "CO3=#.###^^^^" :CO3
            PRINT USING "M^2 * OH ^2 * CO3 =#.###^^^^" :M^2*OH^2*CO3
            PRINT USING "KsoM2OH2CO3 = #.###^^^^" :KsoM2OH2CO3
            PRINT USING "P= #.###^^^^" :P
```

```
            PRINT USING "S= #.###^^^^" :S
            PRINT USING "Ca= #.###^^^^" :Ca
            PRINT

        END IF

! Define the difference function to test for convergence

        LET DIFFUNCTION = M^2 * OH^2 * CO3 - KsoM2OH2CO3

! Check to see if the difference function changed sign or CtM < 0 indicating the correct calcium ion
! concentration was passed

        IF DIFFUNCTION * OLDIFFUNCTION < 0 OR CtM < 0  THEN

            LET TOTAL_SOL = Ca/10
            LET N = TOTAL_SOL
            LET OLDIFFUNCTION = 0
            EXIT FOR

        END IF

! Print intermediate iterative values if debug output option selected

        IF OUTPUT_TYPE = 1 THEN

            PRINT ITERATION; "Ca =";Ca ; "    DIFFUNCTION = ";DIFFUNCTION

        END IF

        LET OLDIFFUNCTION = DIFFUNCTION

! Exit the loop if no solution passed

        IF N = 1 THEN

            LET SOLID$ = "Failed to Converge"
            EXIT SUB

        END IF

    NEXT N

! Final loop to solve for the actual new solubility of CaCO3

! Initialize values

    LET OLDIFFUNCTION = 0

    DO

! Count iterations and check against maximum allowable

        LET ITERATION = ITERATION + 1

        IF ITERATION > MAX_ITERATIONS THEN
```

```
            LET SOLID$ = "Iterations greater than maximum"
            EXIT DO

        END IF

! Supply a value for the calcium ion concentration

        LET Ca = TOTAL_SOL + N * STEP

! Calculate equilibrium values of other species from the supplied calcium ion
! in the subroutine Calculate Values

        CALL  CALCULATE_VALUES

! Calculate M from mass balance equation

        LET P = CtCO3 - S - Ct0CO3 - MgCO3PRECIP
        LET CtM = Ct0M + 2 * P
        LET M = CtM/
(1+BMOH*OH+BMOH2*OH^2+BMHCO3*HCO3+BMCO3*CO3+BMSO4*SO4+BMCl*Cl)

! Define the difference function to test for convergence

        LET DIFFUNCTION = M^2 * OH^2 * CO3 - KsoM2OH2CO3

! Print intermediate iterative values if debug output option selected

        IF OUTPUT_TYPE = 1 THEN

            PRINT  "ITERATION =";ITERATION;"Ca= ";Ca;"DIFFUNCTION =";DIFFUNCTION
            PRINT

        END IF

! Check for convergence by comparing difference function to error criteria

        IF ABS(DIFFUNCTION)/KsoM2OH2CO3 < ERROR_CRITERIA THEN EXIT DO

! If the solution is passed, revise estimate of calcium ion concentration

        IF DIFFUNCTION * OLDIFFUNCTION < 0 OR CtM < 0  THEN

            LET TOTAL_SOL = TOTAL_SOL + N*(STEP-1)
            LET N = N/10
            LET STEP = -1
            LET DIFFUNCTION =0

        END IF

        LET OLDIFFUNCTION = DIFFUNCTION
        LET STEP = STEP + 1

    LOOP

! Calculate equilibrium values from other species after convergence

    LET MOH = M * OH * BMOH
```

```
    LET MOH2aq = M * OH^2 * BMOH2
    LET MHCO3 = M * HCO3 * BMHCO3
    LET MCO3aq = M * CO3 * BMCO3
    LET MSO4aq = M * SO4 * BMSO4
    LET MCl = M * Cl * BMCl
    LET CtSO4 = SO4 + CaSO4aq + MgSO4aq
    IF P > 0 THEN LET SOLID$ = "SOLUTION UNDERSATURATED"
    LET I = 2

END SUB

SUB INPUT

! Interactively select the level of output detail desired

    INPUT PROMPT "Output Type? 1-debug, 2-normal, 3-short: " : OUTPUT_TYPE

    ! Select desired input parameters (concentrations in moles/liter, others in standard units)

    LET ERROR_CRITERIA = 1e-6
    LET MAX_ITERATIONS = 150
    LET Metal$= "Copper"
    LET Ct0M= 0.7
    LET START_pH = 7
    LET END_pH = 11
    LET INTERVAL_pH = .1
    LET GAMMA_2 = 0.651
    LET GAMMA_1 = 0.895
    LET Ct0SO4 = 3.02e-3
    LET Ct0Ca = 7.98e-3
    LET Ct0CO3= 1.175e-2
    LET Ct0Mg = 1.15e-3
    LET Cl = 1.41e-3

END SUB

SUB EQUILIBRATE_CACO3

! Equilibrium constants not associated with the metal of interest

    LET Kw = 10^(-14)
    LET Ka1 = 10^(-6.35)
    LET Ka2 = 10^(-10.33)
    LET KsoCaCO3 = 10^(-8.475)
    LET KsoMgCO3 = 10^(-8.029)
    LET BCaSO4 = 10^(2.31)
    LET BMgCO3 = 10^(2.98)
    LET BMgHCO3 = 10^(1.065)
    LET BMgSO4 = 10^(2.25)
    LET BCaCO3 = 10^(3.15)
    LET BCaHCO3 = 10^(1.015)

END SUB

SUB COPPER

! Equilibrium Constants for Copper
```

```
    LET MWM = 63.546
    LET Ct0M = Ct0M/1E+3/MWM
    LET KsoMOH2 = 10^(-19.36)
    LET KsoMCO3 = 10^(-9.63)
    LET KsoM2OH2CO3 = 10^(-33.18)
    LET BMOH2 = 10^(14.32)
    LET BMOH = 10^(6.00)
    LET BMHCO3 = 10^(2.67)
    LET BMCO3 = 10^(6.73)
    LET BMSO4 = 10^(2.31)
    LET BMCl = 10^(0.43)

END SUB

SUB CADMIUM

! Equilibrium Constants for Cadmium

    LET MWM = 112.40
    LET Ct0M = Ct0M/1E+3/MWM
    LET KsoMOH2 = 10^(-14.29)
    LET KsoMCO3 = 10^(-13.73)
    LET KsoM2OH2CO3 = 10^(10)  ! Value Disabled
    LET BMOH2 = 10^(7.65)
    LET BMOH = 10^(3.92)
    LET BMHCO3 = 10^(2.07)
    LET BMCO3 = 10^(5.40)
    LET BMSO4 = 10^(2.46)
    LET BMCl = 10^(1.98)

END SUB

SUB ACTIVITY_COEFFICIENTS

! Correct equilibrium constants for ionic strength effects

    LET KsoCaCO3 = KsoCaCO3 / (GAMMA_2)^2
    LET Kw = Kw/(GAMMA_1)^2
    LET Ka1 = Ka1/ (GAMMA_1)^2
    LET Ka2 = Ka2/GAMMA_2
    LET KsoMOH2 = KsoMOH2 / GAMMA_2 / (GAMMA_1)^2
    LET KsoM2OH2CO3 = KsoM2OH2CO3 / (GAMMA_2)^3 / (GAMMA_1)^2
    LET KsoMCO3 = KsoMCO3 / (GAMMA_2)^2
    LET KsoMgCO3 = KsoMgCO3 / (GAMMA_2)^2
    LET BCaSO4 = BCaSO4 * (GAMMA_2)^2
    LET BCaCO3 = BCaCO3 * (GAMMA_2)^2
    LET BCaHCO3 = BCaHCO3 * GAMMA_2
    LET BMgHCO3 = BMgHCO3 * GAMMA_2
    LET BMgSO4 = BMgSO4 * (GAMMA_2)^2
    LET BMgCO3 = BMgCO3 * (GAMMA_2)^2
    LET BMOH = BMOH * GAMMA_2
    LET BMOH2 = BMOH2 * GAMMA_2 * (GAMMA_1)^2
    LET BMHCO3 = BMHCO3 * GAMMA_2
    LET BMCO3 = BMCO3 * (GAMMA_2)^2
    LET BMSO4 = BMSO4 * (GAMMA_2)^2
    LET BMCl = BMCl * GAMMA_2
```

```
END SUB

SUB CALCULATE_VALUES

! Calculate equilibrium values of other species from the supplied calcium ion
! in the subroutine Calculate Values

    LET CO3 = KsoCaCO3 / Ca
    LET HCO3 = h * CO3 / Ka2
    LET H2CO3 = h * HCO3 / Ka1
    LET CaCO3aq = BCaCO3 * Ca * CO3
    LET CaHCO3 = BCaHCO3 * Ca * HCO3

! Calculate magnesium ion concentration and associated values assuming in equilibrium with
! magnesium carbonate

    LET Mg = KsoMgCO3 / CO3
    LET SO4 = Ct0SO4 / (1 + BMgSO4 * Mg + BCaSO4 * Ca)
    LET CaSO4aq = BCaSO4 * Ca * SO4
    LET MgSO4aq = BMgSO4 * Mg * SO4
    LET MgCO3aq = BMgCO3 * Mg * CO3
    LET MgHCO3 = BMgHCO3 * Mg * HCO3
    LET CtMg = Mg + MgCO3aq + MgHCO3 + MgSO4aq
    LET MgCO3PRECIP = CtMg - Ct0Mg

! Check the magnesium carbonate assumption.  Recalculate values if assumption not valid.

    IF MgCO3PRECIP > 0 THEN

        LET K = 1 + BMgHCO3 * HCO3 + BMgCO3 * CO3
        LET a = BCaSO4 * BMgSO4 * Ca + BMgSO4
        LET b = K * BCaSO4 * Ca + BMgSO4 * Ct0Mg + K - Ct0SO4 * BMgSO4
        LET c = - Ct0SO4 * K
        LET SO4 = (-b + SQR(b^2 - 4 * a * c))/2/a
        LET CaSO4aq = BCaSO4 * Ca * SO4
        LET Mg = Ct0Mg/(1 + BMgHCO3 * HCO3 + BMGCO3 * CO3 + BMgSO4 * SO4)
        LET MgSO4aq = BMgSO4 * Mg * SO4
        LET MgCO3aq = BMgCO3 * Mg * CO3
        LET MgHCO3 = BMgHCO3 * Mg * HCO3
        LET CtMg = Mg + MgCO3aq + MgHCO3 + MgSO4aq
        LET MgCO3PRECIP = CtMg - Ct0Mg

    END IF

    LET CtCa = Ca + CaCO3aq + CaHCO3 + CaSO4aq
    LET CtCO3 = H2CO3 + HCO3 + CO3 + CaHCO3 + CaCO3aq + MgHCO3 + MgCO3aq
    LET S = CtCa - Ct0Ca

END SUB

SUB OUTPUT

! Print requested output level

    IF OUTPUT_TYPE = 1 OR OUTPUT_TYPE = 2 OR OUTPUT_TYPE = 3 THEN
```

```
        PRINT
        PRINT USING "pH=#.###^^^^" : pH
        PRINT USING "h=#.###^^^^" :h
        PRINT USING "oh=#.###^^^^" :oh
        PRINT "INITIAL METAL CONCENTRATION= ";Ct0M;" M ";METAL$
        PRINT SOLID$
        PRINT "TOTAL METAL CONCENTRATION= ";CtM;"M = " :CtM * MWM * 1e3;" mg/l"
        PRINT USING "M=#.###^^^^" :M
        PRINT USING "MOH2aq=#.###^^^^" :MOH2aq
        PRINT USING "MOH=#.###^^^^" :MOH
        PRINT USING "MHCO3=#.###^^^^" :MHCO3
        PRINT USING "MCO3aq=#.###^^^^" :MCO3aq
        PRINT USING "MSO4aq=#.###^^^^" :MSO4aq
        PRINT USING "MCl=#.###^^^^" :MCl
        PRINT USING "MgCO3_PRECIP=#.###^^^^" :MgCO3PRECIP
        PRINT USING "HCO3=#.###^^^^" :HCO3;" = #.###^^^^" :HCO3 * 61 * 1e3;" mg/l "
        PRINT USING "CO3=#.###^^^^" :CO3
        PRINT USING "Iterations=#.###^^^^" :Iteration

! Check the total aggregate error and flag the output if criteria exceeded

        IF ABS(ERROR_WARNING) > 0.0001 THEN

            PRINT "WARNING! WARNING! WARNING!"
            PRINT "ERROR GREATER THAN MAXIMUM ALLOWED"

        END IF

        PRINT USING "ERROR =#.###^^^^" :ERROR_WARNING

    END IF

    IF OUTPUT_TYPE = 1 OR OUTPUT_TYPE = 2 THEN

        PRINT USING "ERROR CRITERIA#.###^^^^" : ERROR_CRITERIA
        PRINT USING "Ct0Ca= #.###^^^^" :Ct0Ca
        PRINT USING "Ct0CO3= #.###^^^^" :Ct0CO3
        PRINT USING "Ct0Mg= #.###^^^^" :Ct0Mg
        PRINT USING "Ct0SO4= #.###^^^^" :Ct0SO4
        PRINT USING "CtCa= #.###^^^^" :CtCa
        PRINT USING "CtMg= #.###^^^^" :CtMg
        PRINT USING "CtSO4= #.###^^^^" :CtSO4
        PRINT USING "Ca=#.###^^^^" :Ca
        PRINT USING "Mg=#.###^^^^" :Mg
        PRINT USING "CtCO3= #.###^^^^" :CtCO3
        PRINT USING "H2CO3=#.###^^^^" :H2CO3
        PRINT USING "OH=#.###^^^^" :OH
        PRINT USING "SO4=#.###^^^^" :SO4
        PRINT USING "Cl=#.###^^^^" :Cl
        PRINT USING "CaHCO3 =#.###^^^^" :CaHCO3
        PRINT USING "CaCO3 =#.###^^^^" :CaCO3aq
        PRINT USING "CaSO4aq=#.###^^^^" :CaSO4aq
        PRINT USING "MgSO4aq= #.###^^^^" :MgSO4aq
        PRINT USING "MgHCO3= #.###^^^^" :MgHCO3
        PRINT USING "MgCO3aq#.###^^^^" :MgCO3aq
        PRINT USING "S= #.###^^^^" :S
        PRINT USING "P= #.###^^^^" :P
```

```
          PRINT USING "RATIO_MCO3=#.###^^^^" :RATIO_MCO3
          PRINT USING "RATIO_MOH2 =#.###^^^^" :RATIO_MOH2
          PRINT USING "RATIO_M2OH2CO3=#.###^^^^" :RATIO_M2OH2CO3
           PRINT USING "GAMMA1= #.###^^^^" :GAMMA_1
          PRINT USING "GAMMA= #.###^^^^" :GAMMA_2
          PRINT USING "ERROR_BCaSO4= #.###^^^^" :ERROR_BCaSO4
          PRINT USING "ERROR_BCaCO3= #.###^^^^" :ERROR_BCaCO3
          PRINT USING "ERROR_BCaHCO3= #.###^^^^" :ERROR_BCaHCO3
          PRINT USING "ERROR_BMgHCO3= #.###^^^^" :ERROR_BMgHCO3
          PRINT USING "ERROR_BMgSO4= #.###^^^^" :ERROR_BMgSO4
          PRINT USING "ERROR_BMgCO3= #.###^^^^" :ERROR_BMgCO3
          PRINT USING "ERROR_Ka1= #.###^^^^" :ERROR_Ka1
          PRINT USING "ERROR_Ka2= #.###^^^^" :ERROR_Ka2
          PRINT USING "ERROR_KsoCaCO3= #.###^^^^" :ERROR_KsoCaCO3
          PRINT USING "ERROR_KsoMOH2= #.###^^^^" :ERROR_KsoMOH2
          PRINT USING "ERROR_KsoMCO3= #.###^^^^" :ERROR_KsoMCO3
          PRINT USING "ERROR_KsoM2OH2CO3= #.###^^^^" :ERROR_KsoM2OH2CO3
          PRINT USING "ERROR_BMOH= #.###^^^^" :ERROR_BMOH
          PRINT USING "ERROR_BMOH2= #.###^^^^" :ERROR_BMOH2
          PRINT USING "ERROR_BMHCO3= #.###^^^^" :ERROR_BMHCO3
          PRINT USING "ERROR_BMCO3= #.###^^^^" :ERROR_BMCO3
          PRINT USING "ERROR_BMSO4=#.###^^^^" :ERROR_BMSO4
          PRINT USING "ERROR_BMCL= #.###^^^^" :ERROR_BMCL
          PRINT USING "ERROR_CtSO4= #.###^^^^" :ERROR_CtSO4
          PRINT USING "ERROR_MgCO3PRECIP= #.###^^^^" :ERROR_MgCO3PRECIP
          PRINT USING "ERROR_CaCO3_DISSOLVED= #.###^^^^"
:ERROR_CaCO3_DISSOLVED
          PRINT USING "ERROR_METAL_PRECIP= #.###^^^^" :ERROR_METAL_PRECIP

      END IF

END SUB

SUB CHECK

! Check the solution by calculating a checking equilibrium equilibrium constant ( CK)

     LET CKa1 = h * HCO3 / H2CO3
     LET CKa2 = h * CO3 / HCO3
     LET CKsoCaCO3 = Ca * CO3
     LET CKsoMOH2 = M * OH^2
     LET CKsoMCO3 = M * CO3
     LET CKsoM2OH2CO3 = M^2 * OH^2 * CO3
     LET CBCaSO4 = CaSO4aq / Ca / SO4
     LET CBCaCO3 = CaCO3aq / Ca / CO3
     LET CBCaHCO3 = CaHCO3 / Ca / HCO3
     LET CBMgHCO3 = MGHCO3 / Mg / HCO3
     LET CBMgSO4 = MgSO4aq / Mg / SO4
     LET CBMgCO3 = MgCO3aq / Mg / CO3
     LET CBMOH = MOH / M / OH
     LET CBMOH2 = MOH2aq / M / OH^2
     LET CBMHCO3 = MHCO3 / M / HCO3
     LET CBMCO3 = MCO3aq / M / CO3
     LET CBMSO4 = MSO4aq / M / SO4
     LET CBMCl = MCl / M / Cl

! Calculate the relative percentage difference between the checked equilibrium constant and the
```

```
! true value

     LET ERROR_Ka1 = ABS(CKa1-Ka1)/Ka1 * 100
     LET ERROR_Ka2 = ABS(CKa2-Ka2)/Ka2 * 100
     LET ERROR_KsoCaCO3 = ABS(CKsoCaCO3-KsoCaCO3)/KsoCaCO3 * 100
     LET ERROR_KsoMOH2 = ABS(CKsoMOH2-KsoMOH2)/KsoMOH2 * 100
     LET ERROR_KsoMCO3 = ABS(CKsoMCO3-KsoMCO3)/KsoMCO3 * 100
     LET ERROR_KsoM2OH2CO3 = ABS(CKsoM2OH2CO3-KsoM2OH2CO3)/KsoM2OH2CO3
* 100
     LET ERROR_BCaSO4 = ABS(BCaSO4-CBCaSO4)/BCaSO4 * 100
     LET ERROR_BCaCO3 = ABS(BCaCO3-CBCaCO3)/BCaCO3 * 100
     LET ERROR_BCaHCO3 = ABS(BCaHCO3-CBCaHCO3)/BCaHCO3 * 100
     LET ERROR_BMgHCO3 = ABS(BMgHCO3-CBMgHCO3)/BMgHCO3 * 100
     LET ERROR_BMgSO4 = ABS(BMgSO4-CBMgSO4)/BMgSO4 * 100
     LET ERROR_BMgCO3 = ABS(BMgCO3-CBMgCO3)/BMgCO3 * 100
     LET ERROR_BMOH = ABS(CBMOH-BMOH)/BMOH * 100
     LET ERROR_BMOH2 = ABS(CBMOH2-BMOH2)/BMOH2 * 100
     LET ERROR_BMHCO3 = ABS(CBMHCO3-BMHCO3)/BMHCO3 * 100
     LET ERROR_BMCO3 = ABS(CBMCO3-BMCO3)/BMCO3 * 100
     LET ERROR_BMSO4 = ABS(CBMSO4-BMSO4)/BMSO4 * 100
     LET ERROR_BMCL = ABS(CBMCL-BMCL)/BMCL * 100
     LET ERROR_CaCO3_DISSOLVED = ABS(((CtCa-Ct0Ca)-S)/S) * 100
     LET ERROR_METAL_PRECIP = ABS(((Ct0M-CtM)+I * P)/I/P) * 100
     LET ERROR_MgCO3PRECIP = ABS((Ct0Mg-CtMg)+MgCO3PRECIP) * 100
     LET ERROR_CtSO4 = ABS(CtSO4-Ct0SO4)/CtSO4 * 100

! Select the error for the solid in equilibrium

     LET ERROR_SOLID = MIN(ERROR_KsoMOH2,ERROR_KsoMCO3)
     LET ERROR_SOLID = MIN(ERROR_SOLID,ERROR_KsoM2OH2CO3)

! Calculate the aggregate error by summing the individual errors

     LET ERROR_WARNING =
ERROR_Ka1+ERROR_Ka2+ERROR_KsoCaCO3+ERROR_BMOH
     LET ERROR_WARNING =
ERROR_BMOH2+ERROR_BMOH2+ERROR_BMHCO3+ERROR_BMCO3+ERROR_BMSO4
     LET ERROR_WARNING =
ERROR_WARNING+ERROR_BCaSO4+ERROR_CaCO3_DISSOLVED+ERROR_SOLID
     LET ERROR_WARNING =
ERROR_WARNING+ERROR_METAL_PRECIP+ERROR_BMgSO4+ERROR_BMgCO3
     LET ERROR_WARNING =
ERROR_WARNING+ERROR_BCaCO3+ERROR_BCaHCO3+ERROR_BMCL
     LET ERROR_WARNING =
ERROR_WARNING+ERROR_BMgHCO3+ERROR_CtSO4+ERROR_MgCO3PRECIP

END SUB


END
```

APPENDIX 2

```
CODE VERSION: MINTEQK1A     DATE OF CALCULATIONS:  14-MAY-91     TIME:  09:53:39

*****INTERNAL DOCUMENTATION FOR CODE MODIFICATIONS TO THE MINTEQ GEOCHEMICAL MODEL*****
        ONLY THE TWELVE MOST RECENT MODIFICATIONS WILL BE DESCRIBED

             12/01/82 ORIGINAL VERSION OF MINTEQ CODE  COPIED  FROM A. FELMY (MINTEQ.FOR;12);
              PREPARED FOR EPA AND DOCUMENTED IN FELMY
              EPA REPORTS (NTIS PB84-157148 and PB84-157155)
        **   12/17/82 K. KRUPKA ADDED ROUTINES AND FORMATS FOR PRINTING VAX-SYSTEM DATE AND TIME
              FOR THE EXECUTION OF A MINTEQ RUN
        **   12/17/82 K. KRUPKA ADDED PARAMETERS 9 (KKDAV) AND 10(KKTR) RESPECTIVELY: 1) TO JUST USE
              DAVIES EQUATION FOR ACTIVITY COEFFICIENT  CALCULATIONS
              AND 2) TO NOT PRINT THE INITIAL DATA BASE FOR THE AQUEOUS  SPECIES
        **    1/18/83 FROM A. FELMY, IF (ABS(V).GE.38) IN *SOLIDX*, SET C(I) = 0.00
        **    1/28/83 K. KRUPKA ADDED CORRECTIONS TO *SOLIDX* THAT WERE LISTED IN MEMO
              FROM A. FELMY (MEMO NOT DATED, ABOUT 1/25/83)
        **    2/07/83 K. KRUPKA ADDED STATEMENTS TO *IAP* TO BY-PASS TEMPERATURE CORRECTIONS TO
              MIN OR MAX LOG K VALUES THAT EQUAL ZERO
        **    4/11/83 K. KRUPKA ADDED CHANGES FROM 4/5/83 MEMO FROM A. FELMY, WHICH
              DESCRIBES MODIFIICATIONS TO SECTION THAT CALCULATES PERCENT DISTRIBUTION OF COMPONENTS
        **    5/12/83 K. KRUPKA ADDED CHANGES:
              A. C. COWAN MEMO OF 4/18/83 FOR MINTEQ TO HANDLE 50 COMPONENTS; CHANGES TO
                 SUBROUTINES COMMON, CONVERG, MAIN, AND SOLVE
              B. A. FELMY MEMO OF 5/6/83 CONCERNING ROUND-OFF ERROR AND CHANGES TO SUBROUTINE OUTPUT
              C. SUBROUTINE IAP - FOR NO BLANK PAGE AT 52 COUNT
              D. SUBROUTINE INPUT - TO HANDLE MAX OF 12 COMPONENTS IN REACTION OF NEW SPECIES OR SOL

Saturn
Cooling Tower Blowdwon Water
T =  25.00 MG/L     0.00
0 0 1 1 2 0 0 0 0 0
0    0.00    0.00    0.00    0.00
    150   3.200E+02    0.00
    460   2.800E+01    0.00
    500   6.400E+01    0.00
    410   6.500E+00    0.00
    180   5.000E+01    0.00
    732   2.900E+02    0.00
    140   7.050E+02    0.00
    270   5.000E+00    0.00
    580   2.000E+00    0.00
    492   4.000E+00    0.00
    281   3.000E-02    0.00
    471   2.500E-02    0.00
```

```
     30   1.600E+00    0.00
    950   2.500E-02    0.00
    160   2.500E-02    0.00
    600   4.000E-02    0.00
    231   7.000E-01    0.00
    540   2.500E-02    0.00
     20   2.500E-02    0.00
     61   9.500E-03    0.00
    770   6.800E+00    0.00
    330   0.000E+00   -8.00
 H2O HAS  BEEN  INSERTED AS A COMPONENT
  3   2
    330   8.000E+00    0.00
5015001   0.000E+00    0.00
  6   2
2023101   0.000E+00    0.00
5015002   0.000E+00    0.00

INPUT DATA BEFORE TYPE MODIFICATIONS

  ID          NAME         ACTIVITY GUESS     LOG GUESS   ANAL TOTAL
   150   CA                    1.000E+00          0.000    3.200E+02
   460   MG                    1.000E+00          0.000    2.800E+01
   500   NA                    1.000E+00          0.000    6.400E+01
   410   K                     1.000E+00          0.000    6.500E+00
   180   CL                    1.000E+00          0.000    5.000E+01
   732   SO4                   1.000E+00          0.000    2.900E+02
   140   CO3                   1.000E+00          0.000    7.050E+02
   270   F                     1.000E+00          0.000    5.000E+00
   580   PO4                   1.000E+00          0.000    2.000E+00
   492   NO3                   1.000E+00          0.000    4.000E+00
   281   FE+3                  1.000E+00          0.000    3.000E-02
   471   MN+3                  1.000E+00          0.000    2.500E-02
    30   AL                    1.000E+00          0.000    1.600E+00
   950   ZN                    1.000E+00          0.000    2.500E-02
   160   CD                    1.000E+00          0.000    2.500E-02
   600   PB                    1.000E+00          0.000    4.000E-02
   231   CU+2                  1.000E+00          0.000    7.000E-01
   540   NI                    1.000E+00          0.000    2.500E-02
    20   AG                    1.000E+00          0.000    2.500E-02
    61   H3ASO4                1.000E+00          0.000    9.500E-03
   770   H4SIO4                1.000E+00          0.000    6.800E+00
   330   H                     1.000E-08         -8.000    0.000E+00
     2   H2O                   1.000E+00          0.000    0.000E+00
```

```
CODE VERSION:  MINTEQK1A     DATE OF CALCULATIONS:  14-MAY-91     TIME:  09:53:57

TERATIONS DURING SOLVE

    ITER         NAME              TOTAL MOL    DIFF FXN      LOG ACTVTY
     47     CA                    -2.665E-03   -6.149E-05     -3.70330
     48     CA                    -2.665E-03   -4.804E-05     -3.70908
     49     CA                    -2.665E-03   -6.154E-06     -3.69666

 OUTPUT DATA:   ITERATIONS =  49

   ID          NAME              ANAL MOL    CALC MOL    ACTIVITY     LOG ACTVTY      GAMMA       NEW LOGK      DIFF FXN
    150   CA                    7.996E-03   3.073E-04  2.015E-04    -3.69583      0.655605      0.1834     1.433E-08
    270   F                     2.636E-04   2.432E-04  2.167E-04    -3.66407      0.891096      0.0501     6.521E-08
    500   NA                    2.788E-03   2.757E-03  2.467E-03    -2.60791      0.894610      0.0484     6.689E-07
    410   K                     1.665E-04   1.645E-04  1.464E-04    -3.83450      0.889791      0.0507     4.426E-08
    180   CL                    1.412E-03   1.413E-03  1.257E-03    -2.90069      0.889791      0.0507     3.747E-07
    732   SO4                   3.023E-03   2.754E-03  1.747E-03    -2.75761      0.634432      0.1976     2.775E-06
    600   PB                    1.933E-07   9.636E-10  6.139E-10    -9.21193      0.637069      0.1958     1.141E-11
     61   H3ASO4                6.703E-08   4.103E-15  4.114E-15   -14.38572      1.002815     -0.0012     6.373E-11
    540   NI                    4.265E-07   5.110E-09  3.255E-09    -8.48743      0.637069      0.1958     1.873E-11
    492   NO3                   6.461E-05   6.462E-05  5.748E-05    -4.24050      0.889416      0.0509     1.725E-08
     20   AG                    2.321E-07   6.798E-08  6.073E-08    -7.21656      0.893401      0.0490     1.388E-11
    950   ZN                    4.098E-07   3.687E-09  2.406E-09    -8.61868      0.652571      0.1854     0.000E+00
    231   CU+2                  1.103E-05   9.663E-09  6.306E-09    -8.20027      0.652571      0.1854     0.000E+00
    460   MG                    1.153E-03   8.517E-04  5.625E-04    -3.24991      0.660377      0.1802     0.000E+00
    471   MN+3                  4.563E-07   1.196E-24  4.952E-25   -24.30522      0.414148      0.3828     0.000E+00
    281   FE+3                  5.364E-07   9.143E-29  3.787E-29   -28.42175      0.414148      0.3828     0.000E+00
    580   PO4                   2.109E-05   1.946E-13  7.231E-14   -13.14079      0.371617      0.4299     4.235E-22
    770   H4SIO4                7.086E-05   3.526E-05  3.536E-05    -4.45151      1.002815     -0.0012     0.000E+00
    160   CD                    2.226E-07   1.718E-09  1.094E-09    -8.96091      0.637069      0.1958     0.000E+00
     30   AL                    5.939E-05   1.804E-17  7.471E-18   -17.12662      0.414148      0.3828     0.000E+00
      2   H2O                   0.000E+00  -9.320E-05  9.996E-01    -0.00019      1.000000      0.0002     0.000E+00
    330   H                     0.000E+00  -3.945E-03  1.000E-08    -8.00000      0.906696      8.0000     0.000E+00
    140   CO3                   1.177E-02   2.568E-05  1.663E-05    -4.77909      0.647517      0.1887     0.000E+00

  SPECIES:    TYPE  I - COMPONENTS

  ID          NAME          CALC MOL    ACTIVITY    LOG ACTVTY      GAMMA      NEW LOGK       DH
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 150  CA            3.073E-04  0.0002015   -3.69583   0.655605    0.183    0.000
 460  MG            8.517E-04  0.0005625   -3.24991   0.660377    0.180    0.000
 500  NA            2.757E-03  0.0024666   -2.60791   0.894610    0.048    0.000
 410  K             1.645E-04  0.0001464   -3.83450   0.889791    0.051    0.000
 180  CL            1.413E-03  0.0012569   -2.90069   0.889791    0.051    0.000
 732  SO4           2.754E-03  0.0017474   -2.75761   0.634432    0.198    0.000
 140  CO3           2.568E-05  0.0000166   -4.77909   0.647517    0.189    0.000
 270  F             2.432E-04  0.0002167   -3.66407   0.891096    0.050    0.000
 580  PO4           1.946E-13  0.0000000  -13.14079   0.371617    0.430    0.000
 492  NO3           6.462E-05  0.0000575   -4.24050   0.889416    0.051    0.000
 281  FE+3          9.143E-29  0.0000000  -28.42175   0.414148    0.383    0.000
 471  MN+3          1.196E-24  0.0000000  -24.30523   0.414148    0.383    0.000
  30  AL            1.804E-17  0.0000000  -17.12665   0.414148    0.383    0.000
 950  ZN            3.687E-09  0.0000000   -8.61868   0.652571    0.185    0.000
 160  CD            1.718E-09  0.0000000   -8.96091   0.637069    0.196    0.000
 600  PB            9.636E-10  0.0000000   -9.21193   0.637069    0.196    0.000
 231  CU+2          9.663E-09  0.0000000   -8.20027   0.652571    0.185    0.000
 540  NI            5.110E-09  0.0000000   -8.48743   0.637069    0.196    0.000
  20  AG            6.798E-08  0.0000001   -7.21656   0.893401    0.049    0.000
  61  H3ASO4        4.103E-15  0.0000000  -14.38572   1.002815   -0.001    0.000
 770  H4SIO4        3.526E-05  0.0000354   -4.45150   1.002815   -0.001    0.000

 SPECIES:    TYPE  II - COMPLEXES
    ID          NAME        CALC MOL   ACTIVITY   LOG ACTVTY    GAMMA    NEW LOGK      DH
3305801  KH2PO4 -        2.880E-10  0.0000000   -9.58778   0.897042    19.600    -4.520
3305802  H3PO4 AQ        3.614E-16  0.0000000  -15.44078   1.002815    21.699    -2.620
3300020  K OH-           1.127E-06  0.0000010   -5.99820   0.891096   -13.948    13.345
3307700  KH3SIO4 -       4.666E-07  0.0000004   -6.38031   0.892726    -9.880     8.935
3307701  KH2SIO4 -2      1.320E-10  0.0000000  -10.06813   0.647517   -21.428    29.714
7702700  KSIF6 -2        8.627E-29  0.0000000  -28.25520   0.644067    30.371   -16.260
4603300  KMGOH +         1.027E-07  0.0000001   -7.03421   0.900197   -11.738    15.935
4602700  KMGF +          9.006E-06  0.0000081   -5.09398   0.894309     1.869     4.674
4601400  KMGCO3 AQ       8.902E-06  0.0000089   -5.04927   1.002815     2.979     2.022
4601401  KMGHCO3 +       2.602E-05  0.0000232   -4.63390   0.892726    11.444    -2.430
4607320  KMGSO4 AQ       1.743E-04  0.0001748   -3.75752   1.002815     2.249     1.399
4605800  KMGPO4 -        1.760E-10  0.0000000   -9.80169   0.897042     6.636     3.100
4605801  KMGH2PO4 +      5.278E-12  0.0000000  -11.32469   0.897042    21.113    -1.120
4605802  KMGHPO4 AQ      6.731E-10  0.0000000   -9.17069   1.002815    15.219    -0.230
1503300  KCAOH +         5.654E-09  0.0000000   -8.29403   0.898787   -12.552    14.535
1501400  KCAHCO3 +       8.251E-06  0.0000074   -5.12984   0.898787    11.391     1.790
1501401  KCACO3 AQ       4.748E-06  0.0000048   -5.32231   1.002815     3.151     4.030
1507320  KCASO4 AQ       7.151E-05  0.0000717   -4.14444   1.002815     2.308     1.470
1505800  KCAHPO4 AQ      1.767E-10  0.0000000   -9.75161   1.002815    15.084    -0.230
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1505801  KCAPO4  -        4.673E-11  0.0000000  -10.37762  0.897042    6.506    3.100
1505802  KCAH2PO4  +      1.481E-12  0.0000000  -11.87661  0.897042   21.007   -1.120
1502700  KCAF +           4.245E-07  0.0000004   -6.41990  0.895845    0.988    3.798
5001400  KNACO3  -        8.476E-07  0.0000008   -6.11899  0.897042    1.315    8.911
5001401  KNAHCO3  AQ      4.918E-06  0.0000049   -5.30701  1.002815   10.079    0.000
5007320  KNASO4  -        2.408E-05  0.0000216   -4.66552  0.897042    0.747    1.120
5005800  KNAHPO4  -       8.600E-12  0.0000000  -11.11269  0.897042   12.683    0.000
5002700  KNAF  AQ         8.646E-08  0.0000001   -7.06198  1.002815   -0.791    0.000
4107320  KKSO4  -         2.004E-06  0.0000018   -5.74529  0.897042    0.894    2.250
4105800  KKHPO4  -        5.151E-13  0.0000000  -12.33528  0.897042   12.687    0.000
 303300  KALOH  +2        1.180E-14  0.0000000  -14.11680  0.647517   -4.801   11.899
 303301  KAL(OH)2  +      6.610E-12  0.0000000  -11.22700  0.897042  -10.053    0.000
 303302  KAL(OH)4  -      8.340E-09  0.0000000   -8.12737  0.894309  -22.951   44.060
 302700  KALF  +2         2.559E-14  0.0000000  -13.78072  0.647517    7.199    0.000
 302701  KALF2  +         2.200E-12  0.0000000  -11.70480  0.897042   12.797   20.000
 302702  KALF3  AQ        7.942E-12  0.0000000  -11.09886  1.002815   17.019    2.500
 302703  KALF4  -         9.673E-13  0.0000000  -12.06294  0.894309   19.769    0.000
 307320  KALSO4  +        1.528E-17  0.0000000  -16.86426  0.894309    3.069    2.150
 307321  KAL(SO4)2  -     2.122E-18  0.0000000  -17.72187  0.894309    4.969    2.840
 303303  KAL(OH)3  AQ     7.440E-10  0.0000000   -9.12719  1.002815  -16.001    0.000
2813300  KFEOH  +2        3.794E-23  0.0000000  -22.61195  0.644067   -1.999   10.399
2815800  KFEHPO4  +       1.839E-32  0.0000000  -31.78254  0.897042   17.827   -7.300
2817320  KFESO4  +        6.143E-28  0.0000000  -27.25936  0.895845    3.968    3.910
2811800  KFECL  +2        2.232E-30  0.0000000  -29.84245  0.644067    1.671    5.600
2811801  KFECL2  +        9.008E-33  0.0000000  -32.09314  0.895845    2.178    0.000
2811802  KFECL3  AQ       1.011E-36  0.0000000  -35.99383  1.002815    1.129    0.000
2813301  KFEOH2  +        9.017E-19  0.0000000  -18.09211  0.897042   -5.623    0.000
2813302  KFEOH3  AQ       9.473E-19  0.0000000  -18.02231  1.002815  -13.601    0.000
2813303  KFEOH4  -        1.058E-18  0.0000000  -18.02252  0.897042  -21.553    0.000
2815801  KFEH2PO4  +2     4.038E-33  0.0000000  -32.58256  0.647517   25.169    0.000
2812700  KFEF  +2         2.015E-26  0.0000000  -25.88683  0.644067    6.390    2.699
2812701  KFEF2  +         1.253E-25  0.0000000  -24.94990  0.895845   10.848    4.800
2812702  KFEF3  AQ        3.844E-26  0.0000000  -25.41397  1.002815   13.999    5.399
2817321  KFE(SO4)2  -     3.404E-29  0.0000000  -28.51697  0.893401    5.469    4.600
2813304  KFE2(OH)2+4      0.000E+00  1.0000000    0.00000  0.164720   -2.167   13.500
2813305  KFE3(OH)4+5      0.000E+00  1.0000000    0.00000  0.059726   -5.076   14.300
2311400  KCUCO3  AQ       5.616E-07  0.0000006   -6.24935  1.002815    6.729    0.000
2311401  KCU(CO3)2-2      1.851E-08  0.0000000   -7.92844  0.637069   10.026    0.000
2311800  KCUCL  +         2.390E-11  0.0000000  -10.67096  0.897042    0.479    8.650
2311801  KCUCL2  AQ       1.436E-14  0.0000000  -13.84165  0.892726    0.159   10.560
2311802  KCUCL3  -        7.193E-20  0.0000000  -19.19234  1.002815   -2.241   13.690
2311803  KCUCL4  -2       6.281E-25  0.0000000  -24.39303  0.892726   -4.399   17.780
2312700  KCUF  +          2.784E-11  0.0000000  -10.60434  0.644067    1.309    1.620
2313300  KCUOH  +         7.060E-09  0.0000000   -8.20046  0.893401   -7.951    0.000
2313301  KCU(OH)2  AQ     1.313E-06  0.0000013   -5.88065  0.892726  -13.681    0.000
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2313302   KCU(OH)3 -      8.895E-12   0.0000000   -11.09982   0.893401   -26.850    0.000
2313303   KCU(OH)4 -2     2.482E-16   0.0000000   -15.80101   0.637069   -39.404    0.000
2313304   KCU2(OH)2+2     2.731E-11   0.0000000   -10.75942   0.637069   -10.163   17.539
2317320   KCUSO4 AQ       2.243E-09   0.0000000    -8.64788   1.002815     2.309    1.220
2311402   KCUHCO3 +       1.174E-08   0.0000000    -7.97938   0.893401    13.049    0.000
9501800   KZNCL +         9.118E-12   0.0000000   -11.08937   0.892726     0.479    7.790
9501801   KZNCL2 AQ       1.068E-14   0.0000000   -13.97006   1.002815     0.449    8.500
9501802   KZNCL3 -        1.692E-17   0.0000000   -16.82076   0.892726     0.549    9.560
9501803   KZNCL4 -2       1.474E-20   0.0000000   -20.02245   0.644067     0.390   10.960
9502700   KZNF +          8.245E-12   0.0000000   -11.13275   0.893401     1.199    2.220
9503300   KZNOH +         2.952E-10   0.0000000    -9.57887   0.893401    -8.911   13.399
9503301   KZN(OH)2 AQ     3.025E-10   0.0000000    -9.51806   1.002815   -16.900    0.000
9503302   KZN(OH)3 -      1.073E-13   0.0000000   -13.01824   0.893401   -28.350    0.000
9503303   KZN(OH)4 -2     2.384E-18   0.0000000   -17.81845   0.637069   -41.003    0.000
9501804   KZNOHCL AQ      9.982E-12   0.0000000   -10.99956   1.002815    -7.481    0.000
9507320   KZNSO4 AQ       9.829E-10   0.0000000    -9.00629   1.002815     2.369    1.360
9507321   KZN(SO4)2-2     2.197E-11   0.0000000   -10.85390   0.637069     3.476    0.000
9501400   KZNHCO3 +       1.125E-09   0.0000000    -8.99780   0.893401    12.449    0.000
9501401   KZNCO3 AQ       7.962E-09   0.0000000    -8.09777   1.002815     5.299    0.000
9501402   KZN(CO3)2-2     4.456E-09   0.0000000    -8.54685   0.637069     9.826    0.000
1601800   KCDCL +         1.470E-10   0.0000000    -9.88160   0.893401     2.029    0.590
1601801   KCDCL2 AQ       6.863E-13   0.0000000   -12.16229   1.002815     2.599    1.240
1601802   KCDCL3 -        6.095E-16   0.0000000   -15.26398   0.893401     2.448    3.900
1602700   KCDF +          3.342E-12   0.0000000   -11.52498   0.893401     1.149    0.000
1602701   KCDF2 AQ        1.621E-15   0.0000000   -14.78905   1.002815     1.499    0.000
1601402   KCD(CO3)3-4     5.071E-17   0.0000000   -17.07817   0.164720     7.003    0.000
1603300   KCDOH +         1.018E-11   0.0000000   -11.04111   0.893401   -10.031   13.100
1603301   KCD(OH)2 AQ     4.870E-14   0.0000000   -13.31129   1.002815   -20.351    0.000
1603302   KCD(OH)3 -      6.130E-19   0.0000000   -18.26147   0.893401   -33.251    0.000
1603303   KCD(OH)4 -2     7.659E-25   0.0000000   -24.31166   0.637069   -47.154    0.000
1603304   KCD2OH +3       1.345E-19   0.0000000   -19.31202   0.362593    -8.949   10.899
1601803   KCDOHCL AQ      5.407E-12   0.0000000   -11.26579   1.002815    -7.405    4.355
1604920   KCDNO3 +        1.764E-13   0.0000000   -12.80241   0.893401     0.448   -5.200
1607320   KCDSO4 AQ       5.499E-10   0.0000000    -9.25852   1.002815     2.459    1.080
1601400   KCDHCO3 +       5.116E-10   0.0000000    -9.33999   0.893401    12.449    0.000
1601401   KCDCO3 AQ       4.548E-09   0.0000000    -8.34100   1.002815     5.398    0.000
1607321   KCD(SO4)2-2     1.658E-11   0.0000000   -10.97613   0.637069     3.696    0.000
6001800   KPBCL +         3.438E-11   0.0000000   -10.51262   0.893401     1.649    4.380
6001801   KPBCL2 AQ       6.102E-14   0.0000000   -13.21331   1.002815     1.799    1.080
6001802   KPBCL3 -        6.823E-17   0.0000000   -16.21500   0.893401     1.748    2.170
6001803   KPBCL4 -2       5.769E-20   0.0000000   -19.43469   0.637069     1.576    3.530
6001400   KPB(CO3)2-2     1.163E-08   0.0000000    -8.13010   0.637069    10.836    0.000
6002700   KPBF +          2.648E-12   0.0000000   -11.62600   0.893401     1.299    0.000
6002701   KPBF2 AQ        1.044E-14   0.0000000   -13.98007   1.002815     2.559    0.000
6002702   KPBF3 -         1.840E-17   0.0000000   -16.78414   0.893401     3.469    0.000
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6002703  KPBF4 -2        2.677E-21  0.0000000  -20.76821  0.637069    3.296    0.000
6003300  KPBOH +         1.339E-09  0.0000000   -8.92212  0.893401   -7.661    0.000
6003301  KPB(OH)2 AQ     4.639E-11  0.0000000  -10.33232  1.002815  -17.121    0.000
6003302  KPB(OH)3 -      5.977E-14  0.0000000  -13.27246  0.893401  -28.011    0.000
6003303  KPB2OH +3       4.535E-17  0.0000000  -16.78405  0.362593   -5.919    0.000
6004920  KPBNO3 +        5.842E-13  0.0000000  -12.28243  0.893401    1.219    0.000
6007320  KPBSO4 AQ       6.015E-10  0.0000000   -9.21953  1.002815    2.749    0.000
6003304  KPB3(OH)4+2     4.778E-20  0.0000000  -19.51656  0.637069  -23.684   26.500
6001401  KPBCO3 AQ       1.769E-07  0.0000002   -6.75101  1.002815    7.239    0.000
6003305  KPB(OH)4 -2     1.924E-17  0.0000000  -16.91171  0.637069  -39.503    0.000
6007321  KPB(SO4)2-2     8.683E-12  0.0000000  -11.25714  0.637069    3.666    0.000
6001402  KPBHCO3 +       1.811E-09  0.0000000   -8.79103  0.893401   13.249    0.000
5401800  KNICL +         1.148E-11  0.0000000  -10.98913  0.893401    0.448    0.000
5402700  KNIF +          1.576E-11  0.0000000  -10.85151  0.893401    1.349    0.000
5403300  KNIOH +         5.027E-11  0.0000000  -10.34763  0.893401   -9.811   12.420
5403301  KNI(OH)2 AQ     3.243E-12  0.0000000  -11.48782  1.002815  -19.001    0.000
5403302  KNI(OH)3 -      3.639E-15  0.0000000  -14.48798  0.893401  -29.951    0.000
5407320  KNISO4 AQ       1.106E-09  0.0000000   -8.95504  1.002815    2.289    1.520
5401801  KNICL2 AQ       4.677E-14  0.0000000  -13.32882  1.002815    0.959    0.000
5401400  KNIHCO3 +       1.788E-09  0.0000000   -8.79654  0.893401   12.519    0.000
5401401  KNICO3 AQ       4.002E-07  0.0000004   -6.39652  1.002815    6.869    0.000
5401402  KNI(CO3)2-2     1.821E-08  0.0000000   -7.93561  0.637069   10.306    0.000
5407321  KNI(SO4)2-2     1.634E-13  0.0000000  -12.98265  0.637069    1.216    0.000
 201800  KAGCL AQ        1.418E-07  0.0000001   -6.84725  1.002815    3.269   -2.680
 201801  KAGCL2 -        2.000E-08  0.0000000   -7.74794  0.893401    5.319   -3.930
 201802  KAGCL3 -2       3.691E-11  0.0000000  -10.62863  0.637069    5.486    0.000
 201803  KAGCL4 -3       1.353E-13  0.0000000  -13.30933  0.362593    5.951    0.000
 202700  KAGF AQ         3.007E-11  0.0000000  -10.52063  1.002815    0.359   -2.830
 203300  KAGOH AQ        6.054E-12  0.0000000  -11.21676  1.002815  -12.001    0.000
 203301  KAG(OH)2 -      6.792E-16  0.0000000  -15.21695  0.893401  -23.951    0.000
 207320  KAGSO4 -        2.316E-09  0.0000000   -8.68417  0.893401    1.339    1.490
 204920  KAGNO3 AQ       1.785E-12  0.0000000  -11.74706  1.002815   -0.291    0.000
3300611  KH2ASO4 -       2.632E-09  0.0000000   -8.62872  0.893401   -2.194   -1.690
3300612  KHASO4 -2       6.443E-08  0.0000000   -7.38672  0.637069   -8.805   -0.920
3300613  KASO4 -3        2.870E-11  0.0000000  -10.98272  0.362593  -20.156    3.430
3301400  KHCO3 -         3.960E-03  0.0035519   -2.44954  0.897042   10.377   -3.617
3301401  KH2CO3 AQ       7.916E-05  0.0000794   -4.10025  1.002815   16.678   -2.247
3307320  KHSO4 -         1.897E-09  0.0000000   -8.77055  0.894309    2.036    4.910
3302700  KHF AQ          3.189E-09  0.0000000   -8.49507  1.002815    3.168    3.460
3302701  KHF2 -          2.958E-12  0.0000000  -11.57914  0.891096    3.799    4.550
3302702  KH2F2 AQ        2.746E-17  0.0000000  -16.56014  1.002815    6.767    0.000
3305800  KHPO4 -2        2.490E-09  0.0000000   -8.79478  0.644067   12.537   -3.530

SPECIES:   TYPE  III - FIXED SOLIDS
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      ID       NAME              CALC MOL      LOG MOL     NEW LOGK        DH
       2    H2O                -9.320E-05      -4.031       0.000        0.000
     330    H                  -3.945E-03      -2.404       8.000        0.000
 5015001    CALCITE             7.554E-03      -2.122       8.475        2.585

   SPECIES:     TYPE   IV - PRECIPITATED SOLIDS
     ID        NAME              CALC MOL      LOG MOL     NEW LOGK        DH
 3047100    BIXBYITE            2.282E-07      -6.642       0.611       15.245
 8615000    CA-NONTRONIT        2.682E-07      -6.572      20.889        0.000
 7015002    FCO3APATITE         4.393E-06      -5.357     114.400      -39.390
 2003002    DIASPORE            4.241E-05      -4.373      -6.873       24.630
 5016000    OTAVITE             2.151E-07      -6.667      13.740        0.580
 8295000    ZNSIO3              3.857E-07      -6.414      -2.930       18.270
 5023101    MALACHITE           4.555E-06      -5.342       5.180       15.610
 8415000    LEONHARDITE         4.220E-06      -5.375     -16.490       85.360
 5046002    MAGNESITE           8.273E-05      -4.082       8.029        6.169

   SPECIES:     TYPE   V - DISSOLVED SOLIDS
     ID        NAME              CALC MOL      LOG MOL     NEW LOGK        DH
 2003000    ALOH3(A)            3.110E-04      -3.507     -10.380       27.045
 2077000    CHALCEDONY          1.180E-01      -0.928       3.523       -4.615
 8646000    CHRYSOTILE          1.442E-03      -2.841     -32.188       52.485
 8246000    CLINOENSTITE        9.136E-04      -3.039     -11.338       20.015
 2077001    CRISTOBALITE        1.367E-01      -0.864       3.587       -5.500
 6041001    ALUNITE             4.124E-12     -11.385       1.346       -3.918
 8215000    DIOPSIDE            1.843E-04      -3.734     -19.886       32.280
 6041000    ALUM K              4.914E-22     -21.309       5.170       -7.220
 6046000    EPSOMITE            1.353E-04      -3.869       2.140       -2.820
 8646003    SEPIOLITE(C)        1.709E-04      -3.767     -15.913       27.268
 2028100    FERRIHYDRITE        4.861E-10      -9.313      -4.891        0.000
 4128100    FEOH)2.7CL.3        2.226E-05      -4.652       3.040        0.000
 6028100    FE2(SO4)3           0.000E+00     -68.696      -3.580       59.120
 2046000    BRUCITE             9.072E-05      -4.042     -16.792       25.840
 4215000    FLUORITE            8.411E-01      -0.075      10.949       -4.710
 8046000    FORSTERITE          5.632E-08      -7.249     -28.298       48.510
 2003003    GIBBSITE (C)        1.267E-02      -1.897      -8.770       22.800
 2028102    GOETHITE            1.196E-05      -4.922      -0.500       14.480
 6015001    GYPSUM              2.478E-02      -1.606       4.848       -0.261
 4150000    HALITE              8.117E-08      -7.091      -1.582       -0.918
 6003001    AL4(OH)10SO4        1.081E-14     -13.966     -22.700        0.000
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5015003  HUNTITE         2.547E-03      -2.594     29.968     25.760
5046001  HYDRMAGNESIT    2.506E-11     -10.601      8.766     52.210
6050000  JAROSITE NA     6.464E-35     -34.190     11.200     36.180
6041002  JAROSITE K      1.527E-32     -31.816     14.800     31.280
6028101  JAROSITE H      0.000E+00     -38.682     12.100     55.150
8450000  MAGADIITE       3.414E-12     -11.467     14.300      0.000
2028104  MAGHEMITE       5.888E-16     -15.230     -6.386      0.000
7015004  FLUORAPATITE    5.476E-01      -0.262     61.304     14.765
6050001  MIRABILITE      1.376E-07      -6.861      1.114    -18.987
3050000  NATRON          2.062E-09      -8.686      1.311    -15.745
5046003  NESQUEHONITE    3.903E-03      -2.409      5.621      5.789
8646001  PHLOGOPITE      4.312E-31     -30.365    -66.300     86.360
2077002  QUARTZ          3.588E-01      -0.445      4.006     -6.220
8646004  SEPIOLITE(A)    2.321E-07      -6.634    -18.780      0.000
2077003  SIO2(A,GL)      3.689E-02      -1.433      3.018     -4.440
2077004  SIO2(A,PT)      1.815E-02      -1.741      2.710     -3.910
7028100  STRENGITE       6.872E-16     -15.163     26.400      2.030
8646002  TALC            2.455E-03      -2.610    -23.055     35.005
6050002  THENARDITE      1.605E-08      -7.794      0.179      0.572
5050001  THERMONATR      7.584E-11     -10.120     -0.125      2.802
8215001  TREMOLITE       1.593E-04      -3.798    -56.546     96.615
6003000  ALOHSO4         2.216E-09      -8.654      3.230      0.000
2047100  MANGANITE       8.559E-01      -0.068      0.238      0.000
6047100  MN2(SO4)3       0.000E+00     -51.172      5.711     39.060
4123100  MELANOTHALLI    1.855E-18     -17.732     -3.730     12.320
5023100  CUCO3           4.473E-04      -3.349      9.630      0.000
4223100  CUF2            1.235E-15     -14.908      0.620     13.320
4223101  CUF2, 2H2O      1.050E-11     -10.979      4.550      3.650
2023100  CU(OH)2         1.443E-01      -0.841     -8.640     15.250
4123101  ATACAMITE       2.281E-03      -2.642     -7.340     18.690
5123100  CU2(OH)3NO3     1.313E-06      -5.882     -9.240     17.350
6023100  ANTLERITE       2.243E-04      -3.649     -8.290      0.000
6023101  BROCHANTITE     1.259E-03      -2.900    -15.340      0.000
6023102  LANGITE         4.467E-05      -4.350    -16.790     39.610
8615001  PREHNITE        2.375E-09      -8.624    -33.625     78.035
6023103  CUOCUSO4        2.050E-15     -14.688    -11.530     35.575
7023100  CU3(PO4)2       9.282E-15     -14.032     36.850      0.000
7023101  CU3(PO4)2,3W    1.726E-16     -15.763     35.120      0.000
6023104  CUSO4           1.077E-14     -13.968     -3.010     18.140
6023105  CHALCANTHITE    4.799E-09      -8.319      2.640     -1.440
2023102  DIOPTASE        7.051E-04      -3.152     -6.500      8.960
3023100  CUPRICFERIT     1.190E-07      -6.925     -5.880     38.690
4195000  ZNCL2           3.548E-22     -21.450     -7.030     17.480
5095000  SMITHSONITE     4.002E-04      -3.398     10.000      4.360
5095001  ZNCO3, 1H2O     7.278E-04      -3.138     10.260      0.000
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4295000  ZNF2              3.743E-15    -14.427     1.520    13.080
2095000  ZN(OH)2 (A)       8.530E-06     -5.069   -12.450     0.000
2095001  ZN(OH)2 (C)       1.517E-05     -4.819   -12.200     0.000
2095002  ZN(OH)2 (B)       4.275E-05     -4.369   -11.750     0.000
2095003  ZN(OH)2 (G)       4.687E-05     -4.329   -11.710     0.000
2095004  ZN(OH)2 (E)       7.602E-05     -4.119   -11.500     0.000
4195001  ZN2(OH)3CL        4.585E-12    -11.339   -15.200     0.000
4195002  ZN5(OH)8CL2       4.015E-24    -23.396   -38.500     0.000
6095000  ZN2(OH)2SO4       3.196E-12    -11.495    -7.500     0.000
6095001  ZN4(OH)6SO4       2.326E-18    -17.633   -28.400     0.000
5195000  ZNNO3)2,6H2O      2.879E-21    -20.541    -3.440    -5.510
2095005  ZNO(ACTIVE)       1.178E-04     -3.929   -11.310     0.000
2095006  ZINCITE           1.742E-04     -3.759   -11.140    21.860
6095002  ZN3O(SO4)2        4.060E-35    -34.391   -19.020    62.000
7095000  ZN3(PO4),4W       7.973E-21    -20.098    32.040     0.000
2028105  HEMATITE          1.459E-05     -4.836     4.008    30.845
8095000  WILLEMITE         9.575E-06     -5.019   -15.330    33.370
6095003  ZINCOSITE         4.109E-15    -14.386    -3.010    19.200
6095004  ZNSO4, 1H2O       1.561E-11    -10.806     0.570    10.640
6095005  BIANCHITE         2.441E-10     -9.612     1.765     0.160
6095006  GOSLARITE         3.823E-10     -9.418     1.960    -3.300
6015000  ANHYDRITE         1.526E-02     -1.816     4.637     3.769
4116000  CDCL2             8.274E-15    -14.082     0.680     4.470
4116001  CDCL2, 1H2O       8.862E-14    -13.052     1.710     1.820
4116002  CDCL2,2.5H2O      1.504E-13    -12.823     1.940    -1.710
4216000  CDF2              4.908E-14    -13.309     2.980     9.720
2016000  CD(OH)2 (A)       2.036E-07     -6.691   -13.730    20.770
2016001  CD(OH)2 (C)       2.447E-07     -6.611   -13.650     0.000
4116003  CDOHCL            4.152E-08     -7.382    -3.520     7.407
6016000  CD3(OH)4SO4       6.294E-21    -20.201   -22.560     0.000
6016001  CD3OH2(SO4)2      7.792E-24    -23.108    -6.710     0.000
6016002  CD4(OH)6SO4       9.946E-20    -19.002   -28.400     0.000
2016002  MONTEPONITE       8.297E-09     -8.081   -15.120    24.760
7016000  CD3(PO4)2         2.727E-21    -20.564    32.600     0.000
8216000  CDSIO3            3.371E-07     -6.472    -9.060    16.630
6016003  CDSO4             2.407E-12    -11.619     0.100    14.740
6016004  CDSO4, 1H2O       8.675E-11    -10.062     1.657     7.520
6016005  CDSO4,2.7H2O      1.426E-10     -9.846     1.873     4.300
4160000  COTUNNITE         5.711E-11    -10.243     4.770    -5.600
4160001  MATLOCKITE        4.501E-07     -6.347     9.430    -7.950
4160002  PHOSGENITE        6.393E-10     -9.194    19.810     0.000
5060000  CERRUSITE         1.377E-01     -0.861    13.130    -4.860
4260000  PBF2              7.942E-10     -9.100     7.440     0.700
2060000  MASSICOT          7.549E-07     -6.122   -12.910    16.780
2060001  LITHARGE          1.169E-06     -5.932   -12.720    16.380
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2060002  PBO, .3H2O       6.424E-07    -6.192   -12.980     0.000
5060001  PB2OCO3          1.981E-07    -6.703     0.500    11.460
6060000  LARNAKITE        1.254E-05    -4.902     0.280     6.440
6060001  PB3O2SO4         1.608E-09    -8.794   -10.400    20.750
6060002  PB4O3SO4         1.968E-14   -13.706   -22.100    35.070
7060001  CLPYROMORPH      1.115E-04    -3.953    84.430     0.000
7060002  HXYPYROMORPH     2.032E-15   -14.692    62.790     0.000
5060002  PB3O2CO3         3.671E-12   -11.435   -11.020    26.430
7060003  PLUMBGUMMITE     8.232E-15   -14.084    32.790     0.000
7060004  HINSDALITE       1.020E-26   -25.991     2.500     0.000
7060005  TSUMEBITE        1.057E-06    -5.976     9.790     0.000
8260000  PBSIO3           1.039E-05    -4.983    -7.320     9.260
8060000  PB2SIO4          2.315E-11   -10.635   -19.760    26.000
6060003  ANGLESITE        6.614E-05    -4.180     7.790    -2.150
2060004  PB(OH)2 (C)      4.342E-02    -1.362    -8.150    13.990
4160003  LAURIONITE       1.837E-05    -4.736    -0.623     0.000
4160004  PB2(OH)3CL       7.619E-07    -6.118    -8.793     0.000
5060003  HYDCERRUSITE     1.844E-04    -3.734    17.460     0.000
2060005  PB2O(OH)2        2.375E-13   -12.624   -26.200     0.000
6060004  PB4(OH)6SO4      1.966E-13   -12.706   -21.100     0.000
5054000  NICO3            3.745E-07    -6.427     6.840     9.940
2054000  NI(OH)2          5.155E-04    -3.288   -10.800   -30.450
6054000  NI4(OH)6SO4      1.957E-21   -20.708   -32.000     0.000
2054001  BUNSENITE        1.154E-05    -4.938   -12.450    23.920
7054000  NI3(PO4)2        3.599E-21   -20.444    31.300     0.000
6054001  RETGERSITE       6.220E-10    -9.206     2.040    -1.100
6054002  MORENOSITE       1.299E-09    -8.886     2.360    -2.940
8054000  NI2SIO4          1.081E-04    -3.966   -14.540    33.360
4102000  CERARGYRITE      4.293E-01    -0.367     9.750   -15.652
5002000  AG2CO3           7.208E-09    -8.142    11.070    -9.530
4202000  AGF.4H2O         3.703E-12   -11.431    -0.550    -4.270
2002000  AG2O             9.698E-12   -11.013   -12.580    10.430
7002000  AG3PO4           5.748E-18   -17.240    17.550     0.000
6002000  AG2SO4           5.361E-13   -12.271     4.920    -4.250
8450001  ANALCIME         4.402E-04    -3.356    -6.719    22.840
8603000  HALLOYSITE       7.072E-05    -4.150    -8.994    39.730
8603001  KAOLINITE        1.311E-01    -0.882    -5.726    35.280
2003001  BOEHMITE         1.972E-02    -1.705    -8.578    28.130
8450002  LOW ALBITE       2.088E-04    -3.680    -2.592    17.400
8450003  ANALBITE         2.545E-05    -4.594    -3.506    20.000
8641000  MUSCOVITE        2.761E-02    -1.559   -12.990    59.340
8415001  ANORTHITE        5.223E-09    -8.282   -25.430    70.660
8603002  PYROPHYLLITE     3.463E-03    -2.461     1.598     0.000
8415002  LAUMONTITE       6.094E-07    -6.215   -14.460    50.450
8415003  WAIRAKITE        2.373E-11   -10.625   -18.870    63.150
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5046000  ARTINITE          1.319E-05      -4.880      -9.600     28.742
5023102  AZURITE           5.763E-02      -1.239      16.920     23.770
3006100  AS2O5             3.389E-36     -35.470      -6.699      5.405
7060006  PBHPO4            3.526E-07      -6.453      23.900      0.000
7060007  PB3(PO4)2         3.825E-10      -9.417      44.500      0.000
7203000  ALASO4.2W         4.867E-13     -12.313      -4.800      0.000
7215000  CA3(ASO4)26W      6.923E-15     -14.160     -22.300      0.000
7223100  CU3(ASO4)26W      3.368E-12     -11.473      -6.100      0.000
7228100  FEASO4.2W         6.197E-20     -19.208      -0.400      0.000
7254000  NI3(ASO4)28W      1.161E-22     -21.935     -15.700      0.000
7260000  PB3(ASO4)2        6.206E-15     -14.207      -5.800      0.000
7295000  ZN3ASO422.5W      5.273E-21     -20.278     -13.650      0.000
2015000  LIME              3.214E-21     -20.493     -32.797     46.265
2015001  PORTLANDITE       4.254E-11     -10.371     -22.675     30.690
2046001  PERICLASE         1.737E-09      -8.760     -21.510     36.135
3046000  SPINEL            1.456E-10      -9.837     -36.333     89.089
3046001  MAG-FERRITE       1.383E-13     -12.859     -16.765     66.639
4250000  CRYOLITE          3.591E-16     -15.445      31.490    -10.904
8215002  WOLLASTONITE      7.192E-06      -5.143     -12.996     19.498
8215003  P-WOLLSTANIT      1.016E-06      -5.993     -13.846     21.068
8015001  CA-OLIVINE        3.220E-18     -17.492     -37.649     54.695
8015002  LARNITE           1.037E-19     -18.984     -39.141     57.238
8015007  CA3SIO5           0.000E+00     -41.406     -73.867    106.335
8015003  MONTICELLITE      2.142E-10      -9.669     -30.272     49.421
8015005  AKERMINITE        9.630E-20     -19.016     -47.472     76.445
8015004  MERWINITE         1.647E-28     -27.783     -68.543    107.111
8441000  KALSILITE         5.615E-07      -6.251     -12.838     28.919
8441001  LEUCITE           5.167E-05      -4.287      -6.423     22.085
8441002  MICROCLINE        1.173E-03      -2.931      -0.616     12.309
8441003  H SANIDINE        4.199E-04      -3.377      -1.062     14.252
8450004  NEPHELINE         3.944E-07      -6.404     -14.218     33.204
8015006  GEHLENITE         1.205E-23     -22.919     -56.822    116.125
2028103  LEPIDOCROCIT      1.610E-06      -5.793      -1.371      0.000
8650000  NA-NONTRONIT      2.353E-07      -6.628      14.504      0.000
8641002  K-NONTRONITE      1.028E-06      -5.988      15.549      0.000
5015000  ARAGONITE         7.263E-01      -0.139       8.336      2.615
8646005  MG-NONTRONIT      5.949E-01      -0.226      20.589      0.000
5050007  TRONA             9.699E-15     -14.013      11.369     -8.440
7015003  HYDROXYAPATI      3.022E-11     -10.520      39.382     38.924

    SPECIES:    TYPE   VI - SPECIES NOT CONSIDERED

   ID          NAME        CALC MOL      LOG MOL    NEW LOGK        DH
5015002  DOLOMITE          3.134E+00       0.496      17.000      8.290

2023101  TENORITE          1.512E+00       0.180      -7.620     15.240
3301403  CO2(GAS)          2.405E-03      -2.619      18.160     -0.530
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CODE VERSION:  MINTEQK1A     DATE OF CALCULATIONS:  14-MAY-91     TIME:  09:53:58

PERCENTAGE DISTRIBUTION OF COMPONENTS
CA                78.3    PERCENT BOUND IN SPECIES #    150    CA
                   2.1    PERCENT BOUND IN SPECIES #1501400    KCAHCO3 +
                   1.2    PERCENT BOUND IN SPECIES #1501401    KCACO3 AQ
                  18.2    PERCENT BOUND IN SPECIES #1507320    KCASO4 AQ

F                 96.2    PERCENT BOUND IN SPECIES #    270    F
                   3.6    PERCENT BOUND IN SPECIES #4602700    KMGF +

NA                98.9    PERCENT BOUND IN SPECIES #    500    NA

K                 98.8    PERCENT BOUND IN SPECIES #    410    K
                   1.2    PERCENT BOUND IN SPECIES #4107320    KKSO4 -

CL               100.0    PERCENT BOUND IN SPECIES #    180    CL

SO4               91.0    PERCENT BOUND IN SPECIES #    732    SO4
                   5.8    PERCENT BOUND IN SPECIES #4607320    KMGSO4 AQ
                   2.4    PERCENT BOUND IN SPECIES #1507320    KCASO4 AQ

PB                 6.0    PERCENT BOUND IN SPECIES #6001400    KPB(CO3)2-2
                  91.5    PERCENT BOUND IN SPECIES #6001401    KPBCO3 AQ

H3ASO4             3.9    PERCENT BOUND IN SPECIES #3300611    KH2ASO4 -
                  96.0    PERCENT BOUND IN SPECIES #3300612    KHASO4 -2

NI                 1.2    PERCENT BOUND IN SPECIES #    540    NI
                  93.8    PERCENT BOUND IN SPECIES #5401401    KNICO3 AQ
                   4.3    PERCENT BOUND IN SPECIES #5401402    KNI(CO3)2-2

NO3              100.0    PERCENT BOUND IN SPECIES #    492    NO3

AG                29.3    PERCENT BOUND IN SPECIES #     20    AG
                  61.1    PERCENT BOUND IN SPECIES # 201800    KAGCL AQ
                   8.6    PERCENT BOUND IN SPECIES # 201801    KAGCL2 -

ZN                19.6    PERCENT BOUND IN SPECIES #    950    ZN
                   1.6    PERCENT BOUND IN SPECIES #9503300    KZNOH +
                   1.6    PERCENT BOUND IN SPECIES #9503301    KZN(OH)2 AQ
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                     5.2     PERCENT BOUND IN SPECIES #9507320    KZNSO4 AQ
                     6.0     PERCENT BOUND IN SPECIES #9501400    KZNHCO3 +
                    42.2     PERCENT BOUND IN SPECIES #9501401    KZNCO3 AQ
                    23.6     PERCENT BOUND IN SPECIES #9501402    KZN(CO3)2-2
CU+2                29.2     PERCENT BOUND IN SPECIES #2311400    KCUCO3 AQ
                    68.2     PERCENT BOUND IN SPECIES #2313301    KCU(OH)2 AQ
MG                  79.6     PERCENT BOUND IN SPECIES #     460   MG
                     2.4     PERCENT BOUND IN SPECIES #4601401    KMGHCO3 +
                    16.3     PERCENT BOUND IN SPECIES #4607320    KMGSO4 AQ
MN+3               100.0     PERCENT BOUND IN SPECIES #     471   MN+3
FE+3                31.0     PERCENT BOUND IN SPECIES #2813301    KFEOH2 +
                    32.6     PERCENT BOUND IN SPECIES #2813302    KFEOH3 AQ
                    36.4     PERCENT BOUND IN SPECIES #2813303    KFEOH4 -
PO4                  7.4     PERCENT BOUND IN SPECIES #3305801    KH2PO4 -
                     4.6     PERCENT BOUND IN SPECIES #4605800    KMGPO4 -
                    17.4     PERCENT BOUND IN SPECIES #4605802    KMGHPO4 AQ
                     4.6     PERCENT BOUND IN SPECIES #1505800    KCAHPO4 AQ
                     1.2     PERCENT BOUND IN SPECIES #1505801    KCAPO4 -
                    64.4     PERCENT BOUND IN SPECIES #3305800    KHPO4 -2
H4SIO4              98.7     PERCENT BOUND IN SPECIES #     770   H4SIO4
                     1.3     PERCENT BOUND IN SPECIES #3307700    KH3SIO4 -
CD                  22.9     PERCENT BOUND IN SPECIES #     160   CD
                     2.0     PERCENT BOUND IN SPECIES #1601800    KCDCL +
                     7.3     PERCENT BOUND IN SPECIES #1607320    KCDSO4 AQ
                     6.8     PERCENT BOUND IN SPECIES #1601400    KCDHCO3 +
                    60.6     PERCENT BOUND IN SPECIES #1601401    KCDCO3 AQ
AL                  91.6     PERCENT BOUND IN SPECIES #  303302   KAL(OH)4 -
                     8.2     PERCENT BOUND IN SPECIES #  303303   KAL(OH)3 AQ
H2O                 28.9     PERCENT BOUND IN SPECIES #3300020    K OH-
                     2.6     PERCENT BOUND IN SPECIES #4603300    KMGOH +
                    67.2     PERCENT BOUND IN SPECIES #2313301    KCU(OH)2 AQ
H                   95.4     PERCENT BOUND IN SPECIES #3301400    KHCO3 -
                     3.8     PERCENT BOUND IN SPECIES #3301401    KH2CO3 AQ
CO3                 96.1     PERCENT BOUND IN SPECIES #3301400    KHCO3 -
                     1.9     PERCENT BOUND IN SPECIES #3301401    KH2CO3 AQ
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IDX        NAME      AQUEOUS MASS  SORBED MASS
                     --------MOL/KG--------

 150  CA                3.922E-04    0.000E+00
 270  F                 2.527E-04    0.000E+00
 500  NA                2.787E-03    0.000E+00
 410  K                 1.665E-04    0.000E+00
 180  CL                1.413E-03    0.000E+00
 732  SO4               3.026E-03    0.000E+00
 600  PB                1.934E-07    0.000E+00
  61  H3ASO4            6.709E-08    0.000E+00
 540  NI                4.265E-07    0.000E+00
 492  NO3               6.462E-05    0.000E+00
  20  AG                2.321E-07    0.000E+00
 950  ZN                1.886E-08    0.000E+00
 231  CU+2              1.924E-06    0.000E+00
 460  MG                1.070E-03    0.000E+00
 471  MN+3              1.196E-24    0.000E+00
 281  FE+3              2.907E-18    0.000E+00
 580  PO4               3.867E-09    0.000E+00
 770  H4SIO4            3.573E-05    0.000E+00
 160  CD                7.510E-09    0.000E+00
  30  AL                9.101E-09    0.000E+00
   2  H2O               3.906E-06    0.000E+00
 330  H                 4.153E-03    0.000E+00
 140  CO3               4.119E-03    0.000E+00

 CHARGE BALANCE: SPECIATED
       SUM OF CATIONS =  5.284E-03 SUM OF ANIONS   1.127E-02
       PERCENT DIFFERENCE =   3.616E+01   (ANIONS - CATIONS)/(ANIONS + CATIONS)
  NONCARBONATE ALKALINITY =   0.000E+00
IONIC STRENGTH = :  1.221E-02
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CODE VERSION: MINTEQK1A     DATE OF CALCULATIONS:  14-MAY-91     TIME:  09:53:58

 SATURATION INDICES FOR ALL MINERALS AND SOLIDS
   ID        NAME                   SAT INDEX    LOG K    MIN LOGK   MAX LOGK   LOG IAP      DH
 2003000 ALOH3(A)                    -3.507    -10.380    -9.690      0.000      6.873     27.045
 6003000 ALOHSO4                     -8.654      3.230     3.390      3.070    -11.884      0.000
 6003001 AL4(OH)10SO4               -13.966    -22.700     0.000      0.000      8.734      0.000
 6041000 ALUM K                     -21.309      5.170     0.000      0.000    -26.479     -7.220
 6041001 ALUNITE                    -11.385      1.346     0.000      0.000    -12.731     -3.918
 6015000 ANHYDRITE                   -1.816      4.637     0.000      0.000     -6.453      3.769
 5015000 ARAGONITE                   -0.139      8.336     0.000      0.000     -8.475      2.615
 5046000 ARTINITE                    -4.880     -9.600     0.000      0.000      4.720     28.742
 2003001 BOEHMITE                    -1.705     -8.578    -8.065      0.000      6.873     28.130
 2046000 BRUCITE                     -4.042    -16.792     0.000      0.000     12.750     25.840
 5015001 CALCITE                      0.000      8.475     8.560      0.000     -8.475      2.585
 2077000 CHALCEDONY                  -0.928      3.523     0.000      0.000     -4.451     -4.615
 8646000 CHRYSOTILE                  -2.841    -32.188     0.000      0.000     29.347     52.485
 8246000 CLINOENSTITE                -3.039    -11.338   -10.972    -11.632      8.299     20.015
 2077001 CRISTOBALITE                -0.864      3.587     0.000      0.000     -4.451     -5.500
 2003002 DIASPORE                     0.000     -6.873     0.000      0.000      6.873     24.630
 8215000 DIOPSIDE                    -3.734    -19.886     0.000      0.000     16.152     32.280
 5015002 DOLOMITE                     0.496     17.000     0.000      0.000    -16.504      8.290
 6046000 EPSOMITE                    -3.869      2.140     0.000      0.000     -6.009     -2.820
 8646003 SEPIOLITE(C)                -3.767    -15.913     0.000      0.000     12.146     27.268
 2028100 FERRIHYDRITE                -9.313     -4.891    -1.557     -4.996     -4.422      0.000
 4128100 FEOH)2.7CL.3                -4.652      3.040     0.000      0.000     -7.692      0.000
 6028100 FE2(SO4)3                  -68.696     -3.580     0.650      0.000    -65.116     59.120
 7015002 FCO3APATITE                  0.000    114.400     0.000      0.000   -114.400    -39.390
 4215000 FLUORITE                    -0.075     10.949     0.000      0.000    -11.024     -4.710
 8046000 FORSTERITE                  -7.249    -28.298     0.000      0.000     21.049     48.510
 2003003 GIBBSITE (C)                -1.897     -8.770    -8.487     -9.440      6.873     22.800
 2028102 GOETHITE                    -4.922     -0.500     0.000      0.000     -4.422     14.480
 6015001 GYPSUM                      -1.606      4.848     0.000      0.000     -6.454     -0.261
 4150000 HALITE                      -7.091     -1.582     0.000      0.000     -5.509     -0.918
 2028105 HEMATITE                    -4.836      4.008     0.000      0.000     -8.844     30.845
 5015003 HUNTITE                     -2.594     29.968     0.000      0.000    -32.562     25.760
 5046001 HYDRMAGNESIT               -10.601      8.766     0.000      0.000    -19.367     52.210
 6050000 JAROSITE NA                -34.190     11.200     0.000      0.000    -45.390     36.180
 6041002 JAROSITE K                 -31.816     14.800     0.000      0.000    -46.616     31.280
 6028101 JAROSITE H                 -38.682     12.100     0.000      0.000    -50.782     55.150
 8450000 MAGADIITE                  -11.467     14.300     0.000      0.000    -25.767      0.000
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2028104 MAGHEMITE              -15.230     -6.386      0.000      0.000     -8.844      0.000
5046002 MAGNESITE                0.000      8.029      8.279      7.779     -8.029      6.169
6050001 MIRABILITE              -6.861      1.114      0.000      0.000     -7.975    -18.987
3050000 NATRON                  -8.686      1.311      0.000      0.000     -9.997    -15.745
5046003 NESQUEHONITE            -2.409      5.621      5.133      4.546     -8.030      5.789
8646001 PHLOGOPITE             -30.365    -66.300      0.000      0.000     35.935     86.360
2077002 QUARTZ                  -0.445      4.006      0.000      0.000     -4.451     -6.220
8646004 SEPIOLITE(A)            -6.634    -18.780      0.000      0.000     12.146      0.000
2077003 SIO2(A,GL)              -1.433      3.018      0.000      0.000     -4.451     -4.440
2077004 SIO2(A,PT)              -1.741      2.710      0.000      0.000     -4.451     -3.910
7028100 STRENGITE              -15.163     26.400     29.123     26.235    -41.563      2.030
8646002 TALC                    -2.610    -23.055    -18.988    -23.088     20.445     35.005
6050002 THENARDITE              -7.794      0.179      0.000      0.000     -7.973      0.572
5050001 THERMONATR             -10.120     -0.125      0.000      0.000     -9.995      2.802
8215001 TREMOLITE               -3.798    -56.546      0.000      0.000     52.748     96.615
3047100 BIXBYITE                 0.000      0.611      2.226      0.430     -0.611     15.245
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   ID         NAME            SAT INDEX     LOG K    MIN LOGK   MAX LOGK   LOG IAP       DH
2047100 MANGANITE                -0.068     0.238      0.000      0.000     -0.306     0.000
6047100 MN2(SO4)3               -51.172     5.711      0.000      0.000    -56.883    39.060
4123100 MELANOTHALLI            -17.732    -3.730      0.000     -4.450    -14.002    12.320
5023100 CUCO3                    -3.349     9.630      9.650      9.610    -12.979     0.000
4223100 CUF2                    -14.908     0.620      0.000      0.000    -15.528    13.320
4223101 CUF2, 2H2O              -10.979     4.550      0.000      0.000    -15.529     3.650
2023100 CU(OH)2                  -0.841    -8.640      0.000     -9.200      7.799    15.250
4123101 ATACAMITE                -2.642    -7.340     -7.240     -7.490      4.698    18.690
5123100 CU2(OH)3NO3              -5.882    -9.240      0.000     -9.310      3.358    17.350
6023100 ANTLERITE                -3.649    -8.290      0.000     -8.900      4.641     0.000
6023101 BROCHANTITE              -2.900   -15.340    -15.150    -15.500     12.440     0.000
6023102 LANGITE                  -4.350   -16.790      0.000    -17.400     12.440    39.610
2023101 TENORITE                  0.180    -7.620     -7.350     -7.890      7.800    15.240
6023103 CUOCUSO4                -14.688   -11.530      0.000      0.000     -3.158    35.575
7023100 CU3(PO4)2               -14.032    36.850      0.000     36.900    -50.882     0.000
7023101 CU3(PO4)2,3W            -15.763    35.120      0.000      0.000    -50.883     0.000
6023104 CUSO4                   -13.968    -3.010     -2.630     -3.420    -10.958    18.140
6023105 CHALCANTHITE             -8.319     2.640      2.960      2.135    -10.959    -1.440
2023102 DIOPTASE                 -3.152    -6.500      0.000      0.000      3.348     8.960
3023100 CUPRICFERIT              -6.925    -5.880     -5.350      0.000     -1.045    38.690
4195000 ZNCL2                   -21.450    -7.030      0.000     -7.060    -14.420    17.480
5095000 SMITHSONITE              -3.398    10.000     10.810      9.820    -13.398     4.360
5095001 ZNCO3, 1H2O              -3.138    10.260      0.000      0.000    -13.398     0.000
4295000 ZNF2                    -14.427     1.520      0.000      1.080    -15.947    13.080
2095000 ZN(OH)2 (A)              -5.069   -12.450    -12.260    -12.480      7.381     0.000
2095001 ZN(OH)2 (C)              -4.819   -12.200      0.000      0.000      7.381     0.000
2095002 ZN(OH)2 (B)              -4.369   -11.750    -11.320    -11.890      7.381     0.000
2095003 ZN(OH)2 (G)              -4.329   -11.710    -11.190    -11.840      7.381     0.000
2095004 ZN(OH)2 (E)              -4.119   -11.500    -10.950    -11.620      7.381     0.000
4195001 ZN2(OH)3CL              -11.339   -15.200      0.000      0.000      3.861     0.000
4195002 ZN5(OH)8CL2             -23.396   -38.500      0.000      0.000     15.104     0.000
6095000 ZN2(OH)2SO4             -11.495    -7.500      0.000      0.000     -3.995     0.000
6095001 ZN4(OH)6SO4             -17.633   -28.400      0.000      0.000     10.767     0.000
5195000 ZNNO3)2,6H2O            -20.541    -3.440      0.000      0.000    -17.101    -5.510
2095005 ZNO(ACTIVE)              -3.929   -11.310    -11.570    -11.860      7.381     0.000
2095006 ZINCITE                  -3.759   -11.140    -10.990    -11.540      7.381    21.860
6095002 ZN3O(SO4)2              -34.391   -19.020      0.000      0.000    -15.371    62.000
7095000 ZN3(PO4),4W             -20.098    32.040      0.000      0.000    -52.138     0.000
8295000 ZNSIO3                    0.000    -2.930      0.000      0.000      2.930    18.270
8095000 WILLEMITE                -5.019   -15.330    -13.350      0.000     10.311    33.370
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6095003 ZINCOSITE               -14.386    -3.010     0.000    -3.930   -11.376    19.200
6095004 ZNSO4, 1H2O             -10.806     0.570     0.000     0.500   -11.376    10.640
6095005 BIANCHITE                -9.612     1.765     0.000     1.020   -11.377     0.160
6095006 GOSLARITE                -9.418     1.960     0.000     1.870   -11.378    -3.300
5016000 OTAVITE                   0.000    13.740    13.810    11.210   -13.740     0.580
4116000 CDCL2                   -14.082     0.680     0.000     0.470   -14.762     4.470
4116001 CDCL2, 1H2O             -13.052     1.710     0.000     0.000   -14.762     1.820
4116002 CDCL2,2.5H2O            -12.823     1.940     0.000     0.000   -14.763    -1.710
4216000 CDF2                    -13.309     2.980     0.000     0.000   -16.289     9.720
2016000 CD(OH)2 (A)              -6.691   -13.730   -13.610   -14.300     7.039    20.770
2016001 CD(OH)2 (C)              -6.611   -13.650     0.000     0.000     7.039     0.000
4116003 CDOHCL                   -7.382    -3.520    -3.300     0.000    -3.862     7.407
6016000 CD3(OH)4SO4             -20.201   -22.560     0.000     0.000     2.359     0.000
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  ID     NAME               SAT INDEX     LOG K   MIN LOGK   MAX LOGK    LOG IAP         DH
6016001  CD3OH2(SO4)2         -23.108    -6.710      0.000      0.000    -16.398      0.000
6016002  CD4(OH)6SO4          -19.002   -28.400      0.000      0.000      9.398      0.000
2016002  MONTEPONITE           -8.081   -15.120      0.000    -15.740      7.039     24.760
7016000  CD3(PO4)2            -20.564    32.600      0.000      0.000    -53.164      0.000
8216000  CDSIO3                -6.472    -9.060     -7.960      0.000      2.588     16.630
6016003  CDSO4                -11.619     0.100      0.130      0.050    -11.719     14.740
6016004  CDSO4, 1H2O          -10.062     1.657      1.680      1.630    -11.719      7.520
6016005  CDSO4,2.7H2O          -9.846     1.873      1.890      1.860    -11.719      4.300
4160000  COTUNNITE            -10.243     4.770      4.976      4.670    -15.013     -5.600
4160001  MATLOCKITE            -6.347     9.430      0.000      8.600    -15.777     -7.950
4160002  PHOSGENITE            -9.194    19.810     19.940      0.000    -29.004      0.000
5060000  CERRUSITE             -0.861    13.130     13.440     12.830    -13.991     -4.860
4260000  PBF2                  -9.100     7.440      7.570      0.000    -16.540      0.700
2060000  MASSICOT              -6.122   -12.910    -12.790      0.000      6.788     16.780
2060001  LITHARGE              -5.932   -12.720    -12.640    -13.070      6.788     16.380
2060002  PBO, .3H2O            -6.192   -12.980      0.000      0.000      6.788      0.000
5060001  PB2OCO3               -6.703     0.500      0.780      0.000     -7.203     11.460
6060000  LARNAKITE             -4.902     0.280      6.300      0.000     -5.182      6.440
6060001  PB3O2SO4              -8.794   -10.400      0.000      0.000      1.606     20.750
6060002  PB4O3SO4             -13.706   -22.100      0.000      0.000      8.394     35.070
7060001  CLPYROMORPH           -3.953    84.430      0.000     34.510    -88.383      0.000
7060002  HXYPYROMORPH         -14.692    62.790      0.000      0.000    -77.482      0.000
5060002  PB3O2CO3             -11.435   -11.020      0.000      0.000     -0.415     26.430
7060003  PLUMBGUMMITE         -14.084    32.790      0.000      0.000    -46.874      0.000
7060004  HINSDALITE           -25.991     2.500      0.000      0.000    -28.491      0.000
7060005  TSUMEBITE             -5.976     9.790      0.000      0.000    -15.766      0.000
8260000  PBSIO3                -4.983    -7.320     -6.120     -7.640      2.337      9.260
8060000  PB2SIO4              -10.635   -19.760    -19.220    -20.050      9.125     26.000
6060003  ANGLESITE             -4.180     7.790      7.870      0.000    -11.970     -2.150
2060004  PB(OH)2 (C)           -1.362    -8.150      0.000    -13.630      6.788     13.990
4160003  LAURIONITE            -4.736    -0.623     -0.175      0.000     -4.113      0.000
4160004  PB2(OH)3CL            -6.118    -8.793      0.000      0.000      2.675      0.000
5060003  HYDCERRUSITE          -3.734    17.460      0.000      0.000    -21.194      0.000
2060005  PB2O(OH)2            -12.624   -26.200      0.000    -27.100     13.576      0.000
6060004  PB4(OH)6SO4          -12.706   -21.100      0.000      0.000      8.394      0.000
5054000  NICO3                 -6.427     6.840      0.000      0.000    -13.267      9.940
2054000  NI(OH)2               -3.288   -10.800    -10.590    -13.300      7.512    -30.450
6054000  NI4(OH)6SO4          -20.708   -32.000      0.000      0.000     11.292      0.000
2054001  BUNSENITE             -4.938   -12.450      0.000    -12.390      7.512     23.920
7054000  NI3(PO4)2            -20.444    31.300      0.000      0.000    -51.744      0.000
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6054001 RETGERSITE                  -9.206      2.040      0.000      0.000    -11.246     -1.100
6054002 MORENOSITE                  -8.886      2.360      0.000      0.000    -11.246     -2.940
8054000 NI2SIO4                     -3.966    -14.540      0.000      0.000     10.574     33.360
4102000 CERARGYRITE                 -0.367      9.750      0.000      0.000    -10.117    -15.652
5002000 AG2CO3                      -8.142     11.070      0.000      0.000    -19.212     -9.530
4202000 AGF.4H2O                   -11.431     -0.550      0.000      0.000    -10.881     -4.270
2002000 AG2O                       -11.013    -12.580      0.000      0.000      1.567     10.430
7002000 AG3PO4                     -17.240     17.550      0.000      0.000    -34.790      0.000
6002000 AG2SO4                     -12.271      4.920      0.000      0.000    -17.191     -4.250
8450001 ANALCIME                    -3.356     -6.719      0.000      0.000      3.363     22.840
8603000 HALLOYSITE                  -4.150     -8.994      0.000      0.000      4.844     39.730
8603001 KAOLINITE                   -0.882     -5.726      0.000      0.000      4.844     35.280
8415000 LEONHARDITE                  0.000    -16.490      0.000      0.000     16.490     85.360
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   ID          NAME            SAT INDEX     LOG K    MIN LOGK   MAX LOGK    LOG IAP       DH
8450002 LOW ALBITE              -3.680     -2.592     0.000      0.000      -1.088     17.400
8450003 ANALBITE                -4.594     -3.506     0.000      0.000      -1.088     20.000
8641000 MUSCOVITE               -1.559    -12.990     0.000      0.000      11.431     59.340
8415001 ANORTHITE               -8.282    -25.430     0.000      0.000      17.148     70.660
8603002 PYROPHYLLITE            -2.461      1.598     0.000      0.000      -4.059      0.000
8415002 LAUMONTITE              -6.215    -14.460     0.000      0.000       8.245     50.450
8415003 WAIRAKITE              -10.625    -18.870     0.000      0.000       8.245     63.150
5023101 MALACHITE                0.000      5.180     0.000      3.940      -5.180     15.610
5023102 AZURITE                 -1.239     16.920     0.000      0.000     -18.159     23.770
3006100 AS2O5                  -35.470     -6.699     0.000     -9.478     -28.771      5.405
7060006 PBHPO4                  -6.453     23.900     0.000      0.000     -30.353      0.000
7060007 PB3(PO4)2               -9.417     44.500     0.000      0.000     -53.917      0.000
7203000 ALASO4.2W              -12.313     -4.800     0.000      0.000      -7.513      0.000
7215000 CA3(ASO4)26W           -14.160    -22.300     0.000      0.000       8.140      0.000
7223100 CU3(ASO4)26W           -11.473     -6.100     0.000      0.000      -5.373      0.000
7228100 FEASO4.2W              -19.208     -0.400     0.000      0.000     -18.808      0.000
7254000 NI3(ASO4)28W           -21.935    -15.700     0.000      0.000      -6.235      0.000
7260000 PB3(ASO4)2             -14.207     -5.800     0.000      0.000      -8.407      0.000
7295000 ZN3ASO422.5W           -20.278    -13.650     0.000      0.000      -6.628      0.000
2015000 LIME                   -20.493    -32.797     0.000      0.000      12.304     46.265
2015001 PORTLANDITE            -10.371    -22.675     0.000      0.000      12.304     30.690
2046001 PERICLASE               -8.760    -21.510     0.000      0.000      12.750     36.135
3046000 SPINEL                  -9.837    -36.333     0.000      0.000      26.496     89.089
3046001 MAG-FERRITE            -12.859    -16.765     0.000      0.000       3.906     66.639
4250000 CRYOLITE               -15.445     31.490     0.000      0.000     -46.935    -10.904
8215002 WOLLASTONITE            -5.143    -12.996     0.000      0.000       7.853     19.498
8215003 P-WOLLSTANIT            -5.993    -13.846     0.000      0.000       7.853     21.068
8015001 CA-OLIVINE             -17.492    -37.649     0.000      0.000      20.157     54.695
8015002 LARNITE                -18.984    -39.141     0.000      0.000      20.157     57.238
8015007 CA3SIO5                -41.406    -73.867     0.000      0.000      32.461    106.335
8015003 MONTICELLITE            -9.669    -30.272     0.000      0.000      20.603     49.421
8015005 AKERMINITE             -19.016    -47.472     0.000      0.000      28.456     76.445
8015004 MERWINITE              -27.783    -68.543     0.000      0.000      40.760    107.111
8441000 KALSILITE               -6.251    -12.838     0.000      0.000       6.587     28.919
8441001 LEUCITE                 -4.287     -6.423     0.000      0.000       2.136     22.085
8441002 MICROCLINE              -2.931     -0.616     0.000      0.000      -2.315     12.309
8441003 H SANIDINE              -3.377     -1.062     0.000      0.000      -2.315     14.252
8450004 NEPHELINE               -6.404    -14.218     0.000      0.000       7.814     33.204
8015006 GEHLENITE              -22.919    -56.822     0.000      0.000      33.903    116.125
2028103 LEPIDOCROCIT            -5.793     -1.371     0.000      0.000      -4.422      0.000
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8650000 NA-NONTRONIT          -6.628     14.504     16.886     12.122    -21.132      0.000
8641002 K-NONTRONITE          -5.988     15.549     18.334     12.763    -21.537      0.000
8615000 CA-NONTRONIT           0.000     20.889     22.722     19.057    -20.889      0.000
8646005 MG-NONTRONIT          -0.226     20.589     22.165     19.013    -20.815      0.000
5050007 TRONA                -14.013     11.369     11.480      0.000    -25.382     -8.440
7015003 HYDROXYAPATI         -10.520     39.382     44.232      0.000    -49.902     38.924
7015004 FLUORAPATITE          -0.262     61.304     61.400      0.000    -61.566     14.765
8615001 PREHNITE              -8.624    -33.625      0.000      0.000     25.001     78.035
8450005 PHILLIPSITE           -3.651     -1.949      0.000      0.000     -1.702      0.000
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VITA

Mark Oldham Barnett was born in Carrollton, Kentucky on October 20, 1961. Mr. Barnett graduated from the University of Tennessee, Knoxville with a B. S. in Chemical Engineering in August 1985. In September 1985, Mr. Barnett was employed by Newport News Shipbuilding, where he was a certified radiological control engineer (JCJ) specializing in radioactive and mixed waste management. In August 1985, Mr. Barnett entered the graduate program in environmental engineering at the University of Tennessee, Knoxville, earning the M. S. in Environmental Engineering in August 1991. Mr. Barnett is a member of the Chi Epsilon National Civil Engineering Honor Society and the Tau Beta Pi National Engineering Honor Society. Mr. Barnett has been awarded a Department of Education Doctoral Fellowship in Environmental Sciences and Engineering at the University of North Carolina at Chapel Hill.