

Abstract

The objectives of this study were to compare the extent of deposition in drain pipes behind different waterless urinal systems and to determine the nature of those deposits. Urinals were removed from the walls of men's restrooms in different buildings on the University of North Carolina at Chapel Hill campus and at the Raleigh-Durham International Airport, and samples of mineral deposits in the drain pipes were collected. Upon analysis of these mineral deposits, it was determined that the deposits are composed primarily of struvite (magnesium ammonium phosphate). This determination was made using x-ray diffraction analysis, and the results were confirmed using scanning electron microscopy. Additionally, a chemical equilibrium model was used to simulate the hydrolysis of urea in the drain lines behind water-free urinals and determine the equilibrium pH of the system as urea hydrolyzes. This model showed that water-free urinal collection systems are oversaturated with respect to struvite, calcite, and calcium hydroxylapatite, indicating that these minerals are likely to deposit in these systems.

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Chapter 1

Introduction

As water resources become scarcer and water usage becomes more costly, water utilities, homeowners, and facilities managers are considering ways to reduce water consumption. In residential settings, aside from irrigation, water for toilet flushing is typically the largest source of water demand and, depending on the age of the fixtures installed, can constitute over 25% of indoor water use in a single-family home. At many nonresidential sites, such as office buildings, the percentage of water used in restrooms is even higher. As a result, many commercial establishments, residential units, and public institutions have installed water-saving devices in their restrooms in an attempt to use less water. These innovations in plumbing include low-flow faucets, dual-flush toilets, high efficiency urinals, and waterless urinals. This study focuses on non-water urinals, and the mineral deposition that can occur in the pipes behind them.

Currently there are nine manufacturers offering over 30 different models of non-water urinals. These urinals have no flushing mechanism, and most operate using a liquid seal that allows urine to pass through the urinal while preventing odors from emanating into the restroom. Four of the nine manufacturers market urinals that require the liquid sealant to be used within a removable cartridge that fits inside the drain of the urinal. There are three brands available that require no cartridge; in these systems the liquid sealant is poured directly into the urinal.

One of the largest manufacturers of these non-water urinals is Falcon Waterfree Technologies, headquartered in Grand Rapids, Michigan and Los Angeles, California.

Falcon Waterfree manufactures touch-free, water-free urinals and a replaceable liquid sealant cartridge that fits into each urinal. Falcon claims that an average of 40,000 gallons of water per year is conserved with the installation of each Falcon urinal. The cartridges must be replaced on a regular basis (every 3-4 months) because the polymer that serves as the liquid seal dissipates over time, leading to the emission of odors. If water or cleansers are used to rinse or clean the urinal, the liquid seal can be damaged, preventing it from sealing properly. This can also lead to odors in the restroom.

An alternative to the Falcon cartridge and liquid sealant is the Eco Urinal Cartridge (manufactured by Ecotech water, St. Pete Beach, Florida). The Eco cartridge has no liquid seal and fits into the Falcon Waterfree urinal, as well as urinals manufactured by Waterless Co (Vista, CA). It operates using a flexible, rolled-up, rubber tube attached to the drain, which unrolls to allow urine to pass through and then rolls back up to prevent odors from entering into the restroom. When the Eco cartridge is used in place of the Falcon cartridge in the Falcon Waterfree urinal, water and cleansers may be used for rinsing and cleaning the urinal.

In a conventional urinal, urine is diluted with large amounts of water when the system is flushed. The diluted mixture is much less likely to cause odor problems, and its high velocity carries it down the drain, preventing it from standing in the pipe behind the urinal. In water-free urinal systems, a build-up of mineral deposits can occur because urine is allowed to stand in the pipes behind the urinal instead of being diluted and washed away during flushing. On standing, urea present in the urine can hydrolyze, resulting in an increase in pH which can cause precipitates to form. A build-up of these precipitates over time can contribute to plumbing problems, and can be costly to remove.

At the University of North Carolina at Chapel Hill, about 300 Falcon Waterfree urinals were installed in 2003. All of these urinals used Falcon cartridges until 2006. At that time, the Falcon cartridges were replaced with Eco cartridges, and additional conventional urinals were replaced by Falcon urinals with Eco cartridges. Unfortunately, during the past 4 years, the University has experienced problems with the waterless urinal systems. Many odor complaints have been reported, and the maintenance staff have observed problems with the build-up of deposits in the pipes behind the urinals where water-free systems were installed.

The objectives of this study were to compare the extent of deposition between urinals that had used only Falcon cartridges, urinals that had used only Eco cartridges, and urinals that had used both Falcon and Eco cartridges, and to determine the nature of the deposits in the pipes behind the different waterless urinal systems. Identification of the deposits was achieved through Powder X-Ray Diffraction (XRD) analysis and Scanning Electron Microscopy (SEM). A second objective of this study was to develop a chemical equilibrium model to predict the pH increase that would occur as urea hydrolyzes in the pipes behind the urinals and to predict the potential for precipitation to occur.

Chapter 2
Literature Review

2.1 Water Use

Figure 2.1 shows water usage trends in the United States from 1950 to 2000. Estimates show that, from 1975 – 2000, despite the increase in population, total water withdrawals remained relatively constant at 408 billion gallons per day. The majority of this water (about 82%) was used for thermoelectric power and irrigation. Between eleven and twelve percent of the total was withdrawn for public water supply (Hutson et al., 2004).

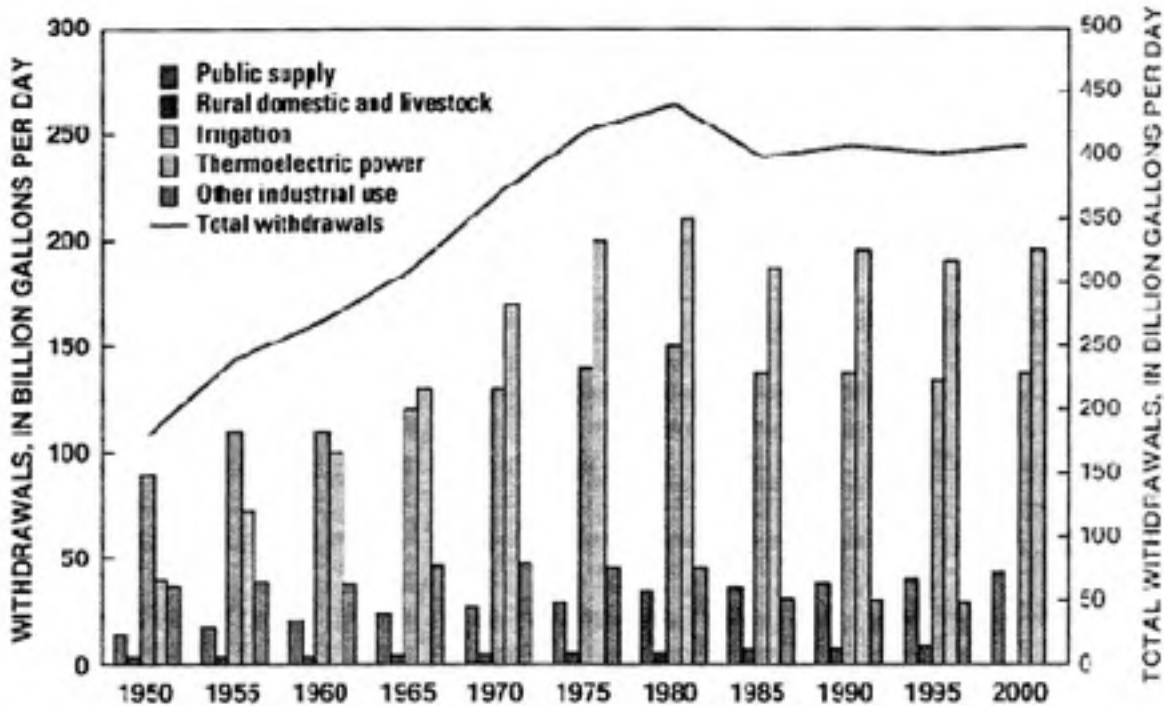


Figure 2.1. Trends in total water withdrawals by water-use category, 1950-2000 (Hutson et al., 2004).

In the United States, total residential water usage is estimated at 26,100 million gallons per day (mgd). Estimated indoor usage for an average non-conserving home is 69.3 gallons per capita per day (gpcd). A summary of indoor usage in a typical single-family home is shown in Figure 2.2. Water used for toilet flushing typically constitutes the largest usage within the household, making up 26.7% of the total, or 18.5 gpcd (Vickers, 2001).

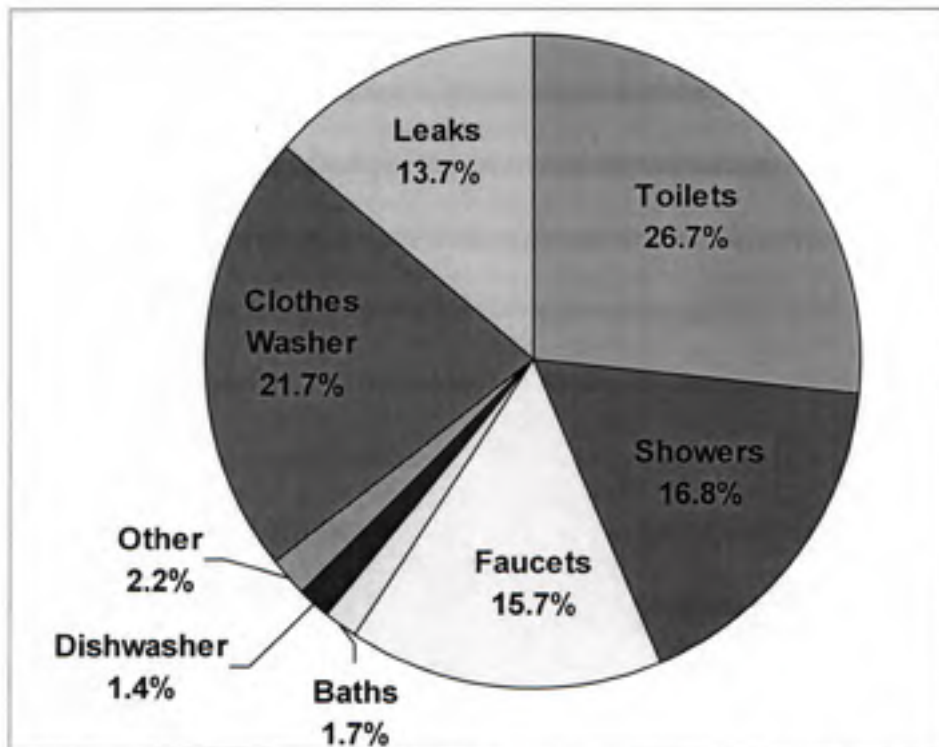


Figure 2.2. Average indoor usage, single family home (adapted from Vickers, 2001)

Water usage in the industrial and commercial sectors in the U.S. (not including mining, agriculture, and thermoelectric power generation) is 27,100 mgd, or about 90 gpcd¹ and 9,590 mgd, or about 32 gpcd, respectively (Solley et al., 2004). Industrial, commercial, and institutional (ICI) water usage varies widely, depending on the type of

¹ gpcd is based on a 2007 population estimate of 301 million, from the US Census Bureau.

facility, and fluctuates more than residential usage based on weather, economic considerations, and building occupancy (Vickers, 2001).

For commercial buildings, water usage can range from 30 to 1,000 gallons of water per employee per day, depending on the type of business; 25 to 50 percent of water usage in commercial establishments can be attributed to water use in restrooms (Dziegielewski et al., 2000; Groves et al., 2007).

2.2 Water Conservation

As seen in Figure 2.1, water demand in the United States rose steadily until the 1980s. At that time, after decreasing slightly, water withdrawals have since remained relatively constant, despite an increase in the U.S. population. Several factors have served to promote water efficiency in recent years, the first being government mandates and incentive programs. Section 2405 of the Energy Policy Act of 1992 mandated a maximum volume of flushing water for all new toilets and urinals manufactured after 1994 (Public Law 102486, 1992). In 1999, an executive order from President Clinton required water audits, water conservation, and the purchase of energy efficient products at government facilities (Clinton, 1999).

Another factor that has encouraged water conservation and water use efficiency is an increase in water and wastewater rates. Many utilities across the United States are implementing conservation-oriented water rates in order to encourage sustainability of water provision, especially during times of drought (Wang et al., 2005). A survey of rates across the United States has shown an annual 4.1% rise in water rates and an annual 4.0% rise in wastewater rates between 1996 and 2006, with the greatest increase in rates (7.0%

and 7.8% for water and wastewater, respectively) occurring between 2004 and 2006 (Raftelis Financial Consulting 2006).

Programs have been implemented throughout the United States in recent years to reduce the amount of water being used. Different water-saving programs employ many of the same techniques, which often include performing a water audit to reduce the amount of unaccounted-for water in a system, re-evaluating water rates to encourage conservation, implementing rebate programs for water-efficient products to be installed in homes, and reducing usage in the ICI sector through elimination of water-wasting processes such as once-through cooling systems.

An example of this is the Massachusetts Water Resources Authority (MWRA), with 2.2 million water customers in the Boston Area, which has successfully reduced demand by one-third. Demand was 336 mgd (about 152 gpcd) in 1987 and the MWRA predicted that, by 2007, demand would rise to 450 mgd (about 205 gpcd). MWRA's three-fold plan to reduce water demand included reducing leaks in their distribution system, concentrating on reductions in the ICI sector through water audits and more efficient water-using processes, and encouraging demand reduction in the residential sector by assisting customers with the installation of water-saving devices in their homes. By 1997, demand was reduced to 256 mgd (116 gpcd) and in 2007, it reached 214 mgd (97 gpcd), the lowest water demand for that service area since 1911 (Brzozowski, 2008; MWRA 2008).

The city of Albuquerque, NM implemented a similar program after discovering that the aquifer used for the City's water was being depleted faster than it was being replenished. In 1994, the plan called for a 30 percent reduction in water demand by

2004. Steps taken by the City to reduce demand included reducing leaks in the distribution system, experimenting with water rates, offering a rebate program to households that install low-flow toilets, and reducing ICI water usage through more efficient processes. The goal was exceeded, and demand was reduced by 33 percent. This success prompted an extension of the program, calling for a 40 percent reduction in water demand from 1994 levels by the year 2014 (Anderson, 2005).

2.3 Water Conservation in Lavatories

It is clear that a large portion of water being used in the residential and ICI sectors in the United States can be attributed to water use in lavatories, associated with sinks and toilets. Table 2.1 shows the water use rate of these devices.

Table 2.1. Estimated water use in lavatories (Adapted from Vickers, 2001)

Year Manufactured	Water Use Rate		
	Faucets (gpm [*])	Toilets (gpf [†])	Urinals (gpf [†])
pre 1980s	3.0 - 7.0	5.0 - 7.0	5.0
1980-1994	2.5 - 3.0	3.5 - 4.5	1.5 - 4.5
1994-present	1.5 - 2.5	1.0 - 1.6	0.0 - 1.0
Current Federal Standard	2.2	1.6	1.0

* gallons per minute

† gallons per flush

In the U.S., there are approximately 222 million residential lavatory faucets currently installed and an additional 25 million purchased each year. Faucets in residential lavatories and kitchens account for about 15.7 percent or 1.1 trillion gallons of indoor water use each year (US EPA, 2007b). In 1998 the U.S. Department of Energy adopted a standard of 2.2 gpm at 60 psi for lavatory faucets. This standard can be found in the Code of Federal Regulations, 10 CFR Part 430.32(o). In addition to installing low-flow faucets, water usage in restrooms can also be lowered through the repair of leaky

faucets and the addition of faucet retrofits, such as aerators and flow restrictors. Aerators are easy to install, inexpensive, and can reduce flow to a maximum of 0.5 to 1.0 gpm. When aerators are not a feasible option, flow restrictors can be installed that will restrict flow rates to a maximum of 0.5-1.5 gpm (Groves, 2007).

The main target of many conservation and rebate programs is water-saving through toilet retrofits or replacements. Water for flushing residential toilets accounts for about 27 percent of indoor residential water usage—an amount equal to over 2.1 trillion gallons per year. Currently, there are approximately 222 million residential toilets in the U.S. (US EPA 2007a) The majority of toilets use 5.0, 3.5, or 1.6 gallons per flush (gpf) (Groves, 2007). Existing federal regulations state that all gravity tank, flushometer tank, and electromechanical hydraulic toilets should have a maximum flush volume of 1.6 gpf. This requirement can be found in the Code of Federal Regulations, 10 CFR Part 430.32 (q). Additional federal regulations require that toilets sold in the U.S. be certified and tested as specified by the requirements of American Society of Mechanical Engineers (ASME) A112.19.2 (EPA 2007a). Retrofits such as displacement devices, replacing the flush valve with an early-closure device, or installing a dual flush adapter, are successful approaches for limiting the amount of flushing water used. These retrofits are most effective for older toilets, especially those using more than 3.5 gpf (Groves, 2007).

Many conservation programs have not targeted urinals as a major source of water conservation because they are only applicable to commercial and institutional settings. However, by replacing older urinals that use more than 2 gallons per flush, over 1000 gallons per urinal per year can be saved (Vickers, 2001). Of the approximately 12 million urinals currently installed in the U.S., up to 80 percent (EPA 2008) exceed the

current regulatory standard of 1.0 gpf as defined by the Energy Policy Act of 1992 (Public Law 102486), which is found in the Code of Federal Regulations, 10 CFR Part 430.32(r). Since the Federal standards were enacted, a number of manufacturers have begun to offer urinals which use 0.5 gpf or less. These are widely recognized by the plumbing industry as High Efficiency Urinals (HEUs). Another relatively new product is the 0 gpf, non-water or water-free urinal, discussed in detail in the following section.

2.4 Non-water Urinals

The non-water urinal is defined by the American National Standards Institute (ANSI) as “a plumbing fixture that is designed to receive and convey only liquid waste through a trap seal into the gravity drainage system without the use of water for such function” (ANSI, 2004). Non-water urinals first gained popularity in Europe and, by the mid-1990s, were being installed with greater frequency in the U.S. and other countries. In addition to the water-saving benefits of these non-water urinals, they are simpler to operate because there is no flushing mechanism. In most cases, they can also easily replace existing conventional urinals that are connected to standard two-inch drain lines.

Most non-water urinal fixtures are regulated by the ASME/ANSI standard A112.19.19 for vitreous china plumbing fixtures (ASME, 2006). However, some urinals are regulated by IAPMO/ANSI Z124.9, which sets forth guidelines for plastic urinals (ANSI 2004). Most drainage lines from urinals are two inches in diameter. Plumbing codes for these drainage lines can vary, depending on the State and the size of pipe. For example, in North Carolina, a two-inch drain line requires a slope of one-quarter inch per foot (NC Building Code, 2002). The design and installation of the drain line is important

for non-water urinals due to the potential build-up of mineral precipitates, as discussed below.

There are at least nine manufacturers currently marketing non-water urinals. The different models use a variety of technologies. The most common technology used, especially in the United States, is a urinal with a replaceable cartridge which operates using a liquid seal that is contained within the cartridge. Figure 2.3 shows an example of one liquid seal cartridge, available from Falcon Waterfree (Los Angeles, CA).

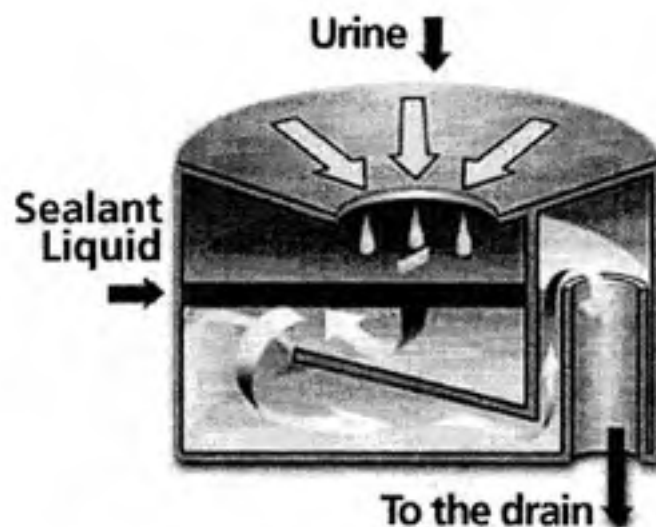


Figure 2.3. Falcon Waterfree replaceable cartridge (Source: Falcon Waterfree, 2008)

Falcon Waterfree offers eight different urinal models, five for the United States, and three international models. As shown in Figure 2.3, urine enters at the top of the cartridge, and passes through the liquid seal, which floats on top of the urine. The urine fills up the bottom portion of the cartridge, and exits to the drain. Waterless Company, another large, non-water urinal company (Vista, CA) produces six different models which also operate using a liquid seal contained within a removable cartridge. Two other

manufacturers offer non-water urinals which use the liquid seal cartridge technology: Armitage Shanks (Hull, UK) has one model and Zero Flush (Kissimmee, FL) has three models available.

Another common type of non-water urinal configuration is a urinal which operates using a liquid seal, but which does not have a replaceable cartridge. Instead of being contained inside a cartridge, the liquid seal is poured directly into the trap (Figure 2.4). Manufacturers offering this non-water urinal technology include Duravit (Hornberg, Germany) which offers one model, Kohler (Kohler, WI) which offers three models, and seven models are sold by Uridan (Haderslev, Denmark).

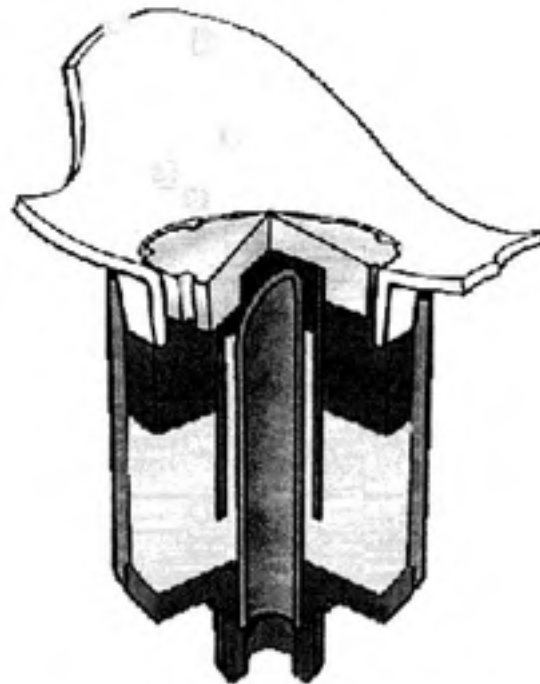


Figure 2.4 Uridan waterfree liquid seal with no replaceable cartridge (source: Uridan 2008)

One very important aspect of the liquid seal is that water and cleansers cannot be used with these urinals. Pouring water into the urinal will damage the liquid seal. When

the seal becomes damaged, it no longer serves as an adequate barrier between the drain-lines and the restroom, and odors will become a problem.

Additionally, there are a few models of non-water urinals being sold that do not use liquid sealant technology. One example is the buoyancy body design used by Urimat (Hundsangen, Germany). The design is shown in Figure 2.5. The system still uses a cartridge; however, there is no liquid seal. Instead, a float assembly moves down when urine is introduced, allowing urine to pass through, and then floats up and seals the inlet to prevent odors.

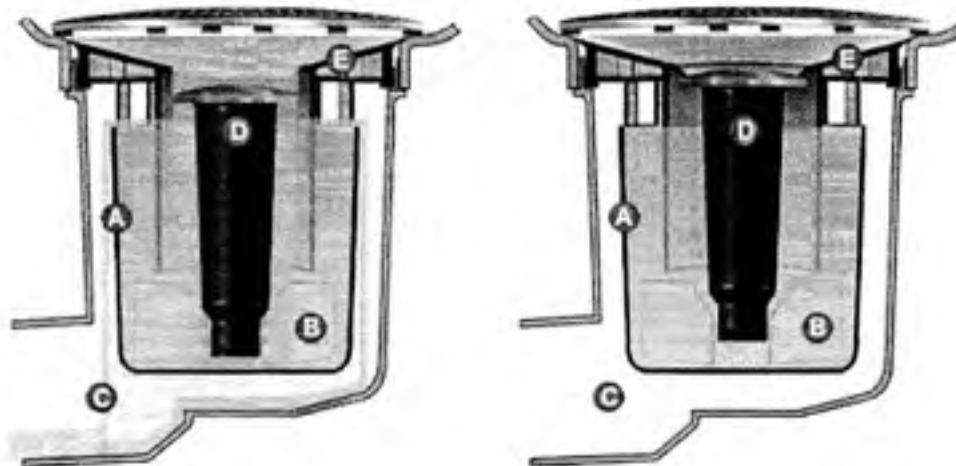


Figure 2.5. Urimat Siphon with hydrostatic float assembly. The element (A) is inserted into the Urimat urinal. Urine flows into the container (B), and from there overflows into (C) which leads to the drain-line. The inlet is then sealed by the float assembly (D). The sealing rim (E) prevents odors from emanating into the restroom (Source: Urimat, 2008)

Another design is marketed by Sanitec (Helsinki, Finland) and employs a stainless steel discharge element which is placed in the urinal. The one-way valve allows urine to pass through, without the need for flushing water.

All of the companies previously mentioned manufacture and sell both the urinal and the cartridge or discharge element that corresponds with their particular urinal. In most

cases, the cartridge from one manufacturer cannot be used in the urinal of another manufacturer due to differences in design. One exception is the Eco Urinal Cartridge (Ecotech Water, St. Pete Beach, FL). The Eco cartridge (shown in Figure 2.6) is designed to fit into the Falcon Waterfree urinal, as well as urinals manufactured by Waterless Co. It has no liquid seal but operates using a flexible, rolled-up, rubber tube attached to the drain. The tube unrolls to allow urine to pass through and then rolls back up to prevent odors from entering into the restroom. Unlike urinals using a liquid sealant, when the Eco cartridge is used in place of the Falcon cartridge in the Falcon Waterfree urinal, water and cleansers may be used for rinsing and cleaning the urinal.

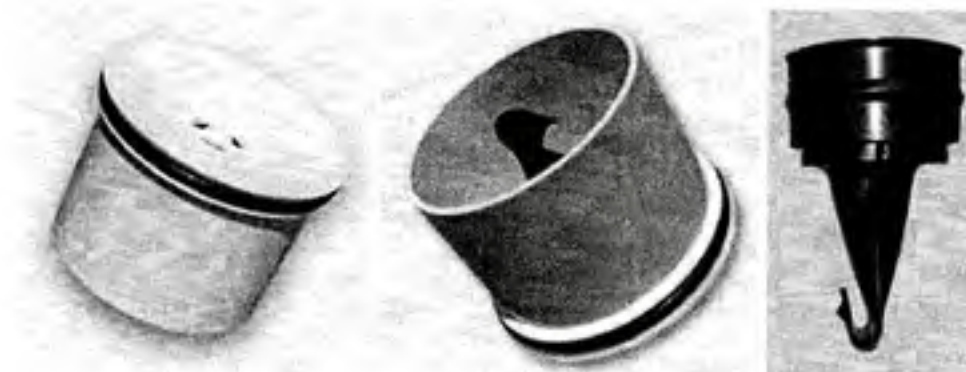


Figure 2.6. Eco Urinal Cartridge and check valve (Source: Ecotech, 2008)

As described above, there are many non-water urinal options available. However, some types of non-water urinals may be prohibited by building codes. For example, the North Carolina building code was recently changed, and permits only non-water urinals which have liquid sealant contained in a removable trap [cartridge] (NC Building Code, 2006). Under this new regulation, urinals manufactured by Duravit, Kohler, Uridan, Urimat, and Sanitec are excluded. The Eco Urinal Cartridge, which fits into the Falcon

Waterfree and the Waterless Co urinals, is also prohibited under the North Carolina building code.

Although the water-saving attributes of non-water urinals are obvious, some users and building administrators have encountered problems with them. There are concerns that use of non-water urinals may cause unpleasant odors in restrooms, especially if the urinal cartridges are not maintained and replaced properly. Another problem is that the absence of flushing water in non-water urinals may cause the build-up of mineral deposits in drain lines, which could ultimately affect the performance of the urinal. Mineral deposition in non-water urinals is the main focus of this report, and is discussed in detail in Chapters 3, 4, and 5.

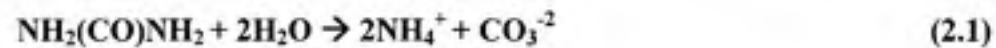
2.5 Urine Chemistry

As mentioned in the previous section, a major concern with non-water urinals is the potential for build-up of mineral deposits in the drain lines. In order to appreciate the circumstances under which these deposits might form, it is important to understand the chemistry of urine that leads to these mineral deposits. Urine contains a variety of components, including the major species listed in Table 2.2 (after Udert et al., 2003b). It is these species that are of primary concern when exploring the feasibility of separating urine from wastewater and in understanding the problem of mineral deposition in urine-collecting systems.

Table 2.2. Average concentration of major species present in urine (adapted from Udert 2003b)

	Formula	Average Conc (mol/L)	Standard Deviation (\pm)	CV %
Ammonia	NH ₃	0.034	0.010	29
Phosphate	PO ₄ ⁻³	0.024	0.03	14
Calcium	Ca ⁺²	0.0046	0.0010	22
Magnesium	Mg ⁺²	0.0039	0.0008	21
Sodium	Na ⁺	0.12	—	—
Potassium	K ⁺	0.056	—	—
Carbonate	CO ₃ ⁻²	0	—	—
Sulfate	SO ₄ ⁻²	0.016	0.005	29
Chloride	Cl ⁻	0.11	—	—
Oxalate	(COO) ₂ ⁻²	0.00023	0.6e-04	26
Citrate	C ₃ H ₅ (COO) ₃ ⁻³	0.0026	0.0010	38
Urea	(NH ₂) ₂ CO	0.27	0.05	20
pH		6.2	0.5	8

In non-water urinals, where no flushing water is added, the chemical composition of urine can be altered due to the hydrolysis of urea. Urea hydrolysis, shown in Equation 2.1, occurs when the enzyme urease hydrolyzes urea to release ammonia and carbonate.



Urease is produced by a variety of different microorganisms. Urease-positive organisms are ubiquitous, being found in soil, water, the human intestinal system, and urine-collecting systems (Udert et al. 2003a). Some conditions, such as nitrogen availability, urea concentration, temperature, and pH, can affect the synthesis of urease by microorganisms, but many bacteria produce the enzyme at a relatively constant rate.

When urea hydrolyzes, the release of ammonia and carbonate causes the pH to increase. This pH increase, along with the increase in ammonia and carbonate concentrations, can lead to over-saturation with respect to several different minerals. Struvite (MgNH₄PO₄), calcium carbonate (CaCO₃), and calcium hydroxylapatite

$(Ca_5(PO_4)_3(OH)_2)$ are the most likely precipitates to form in a water-free system. However, even if the urine is diluted with tap water, such as occurs in low-flush systems, precipitation of these solids may also occur (Udert 2003a,b).

The formation of struvite has been well researched. For example, in the medical field, it is known that the hydrolysis of urea can be responsible for causing the formation of urinary stones (Mobley & Hausinger, 1989). Other studies have sought to better understand the formation of struvite in order to prevent operational problems that occur in high nutrient waters, such as anaerobic digester supernatant and urine storage and conveyance systems (Aage et al. 1997, Bhuiyan 2007a, Doyle et al 2002b, Ohlinger et al. 1998, Stratful et al. 2001, Udert et al. 2003a,b). Research has also been undertaken to investigate the potential of struvite to serve as a fertilizer by processing anaerobic digester supernatant from wastewater treatment plants and source-separated urine collection systems. Struvite exhibits desirable properties, such as low solubility and low heavy metal content that make it an attractive option as a potential fertilizer (Doyle & Parsons, 2002a). The most promising aspect of struvite for use as a fertilizer is its phosphorus content. Jaffer et al. (2002) showed that 97% phosphorus removal as struvite could be achieved in a wastewater treatment plant's centrifuge liquor processing stream. Struvite precipitation has also been shown to facilitate phosphorus recovery from source-separated urine. Lind et al. (2000) demonstrated that with small amounts of MgO added to urine, most of the phosphorus could be precipitated, primarily as struvite.

Chapter 3

Experimental Procedures

One conventional urinal and eight water-free urinals were removed from the walls of several men's restrooms on the UNC campus and at Raleigh-Durham International Airport. The drain pipe behind each urinal was inspected and photographed and, when possible, a telescoping camera was used to view deposits deeper in the pipe. In pipes having a significant amount of deposition, a sample of the deposit was collected, sterilized, dried, ground, and analyzed using powder x-ray diffraction (XRD) analysis and scanning electron microscopy (SEM). In addition to these analyses, a chemical equilibrium model was developed to simulate pH changes accompanying the hydrolysis of urea that takes place in the pipes, and to predict the over-saturation potential with respect to several minerals, most notably struvite and calcium hydroxylapatite.

3.1 Collection of Samples

Of the nine sites that were inspected, seven were located on campus at the University of North Carolina (UNC) and two were located at the Raleigh-Durham International Airport (RDU). Locations were chosen so that different types of waterless systems could be assessed. Of the urinals that were removed, four had used only Falcon liquid seal cartridges, two had switched from using Falcon cartridges to Eco cartridges, two had used only Eco cartridges, and one was a conventional flush urinal. In addition to the different varieties of urinal systems, the sites inspected varied widely with respect to frequency of usage. In a very high traffic facility such as the RDU Airport, a urinal may

have as much as several hundred uses per day, while in a low traffic facility on campus such as sparsely populated buildings, a urinal may have less than 10 uses per day. Table 3.1 presents a summary of the sampling locations selected in this study.

Table 3.1 Summary of sampling locations

Building Name Sample Name	Urinal System	Facility Usage	Deposit Found
Giles Horney-- Conventional	Conventional--flush	Low Usage	None
Giles Horney-- Water Saving	Falcon-3 yr, Eco-1 yr	Low Usage	Substantial
Energy Services	Eco--1 yr	Very Low Usage	None
Bondurant	Eco--1 yr	High Usage	Very little
R.B. House	Falcon-3 yr, Eco-1 yr	High Usage	Some
FedEx Global-- 1st Floor	Falcon--6 months	High Usage	Substantial
FedEx Global-- 4th Floor	Falcon--6 months	Very Low Usage	Some
RDU airport-- Terminal A	Falcon--6 years	Very High Usage	Substantial
RDU airport-- Operations	Falcon--4 years	Low Usage	Substantial

To allow access to the drain line behind each urinal, UNC facilities personnel removed each urinal from the wall. After breaking the seal around the outer edge of the urinal using a knife, the urinal was lifted off the wall. At RDU, this was done by UNC Facilities personnel with the assistance of RDU staff and security. In most restrooms, the drain pipe from the urinal consists of a one- to two-foot cast iron pipe that runs horizontally behind the urinal before joining the main vertical drain line. This short horizontal section of pipe was accessible for inspection and for collecting samples of deposited material.

When the horizontal drain line was exposed, photographs were taken to document the amount of deposit present. In several of the sampling locations, a telescoping camera was used to view the amount of deposit present deeper into the drain pipe. Table 3.1 indicates the extent of mineral deposition found at each of the sampling locations. A small metal spatula was used to scrape deposit from the drain line. The material collected was stored in a sealed plastic vial.

In one of the buildings on the UNC campus (FedEx Global), modified Falcon urinals had been installed in 2007. The modified urinals were identical to the traditional Falcon urinals, except for a nine-inch plastic tube that extends from the back of the urinal and fits snugly inside the horizontal cast iron drain line. When these modified Falcon urinals were inspected, samples of deposited material were taken both from the extension tube and from the cast iron drain line.

3.2 Analysis of Samples

As soon as possible after collection (usually within 3 days), samples were autoclaved at 121°C for 18 minutes. Sterilized samples were subsequently placed in a drying oven at 104°C until completely dry, and cooled in a desiccator. The dry samples were then ground into a powder using a mortar and pestle. Powdered samples were stored in glass vials at 4°C.

Seven of the samples were subjected to powder x-ray diffraction (XRD) analysis. The analysis was performed in the Department of Chemistry at UNC with the assistance of Dr. Peter White, using a Rigaku Multiflex powder diffractometer with Nickel filtered Cu K α radiation. The settings used for this analysis were 40 kV and 40 mA.

Following the XRD analysis, an effort was made to match the sample patterns with known patterns of minerals from the Department's XRD database. However, none of the minerals of interest were present in the database. As a result, the samples were sent to Kirk Scheckel at the US EPA National Risk Management Research Laboratory in Cincinnati, OH for further XRD analysis and identification

Three samples were analyzed using Scanning Electron Microscopy (SEM). Analysis was performed in UNC's Department of Geology laboratory using a Stereoscan 440 Leica electron microscope with Revolution software, with the assistance of Dr. Allen Glazner and his students. The beam current was 400 uAmps, the electron high tension (EHT) was 15.00 kV, and the I-probe setting was 200 pA.

3.3 Chemical Equilibrium Modeling

Table 3.2 gives the average composition of the major dissolved species in urine. As shown, urine contains an average of 0.27 mol/L of urea.

Table 3.2 Concentration of major species present in urine (from Udert et al., 2003)

Name	Formula	Avg Concn (mol/L)
Ammonia	NH_3	0.034
Phosphate	PO_4^{-3}	0.024
Calcium	Ca^{+2}	0.0046
Magnesium	Mg^{+2}	0.0039
Sodium	Na^+	0.12
Potassium	K^+	0.056
Carbonate	CO_3^{-2}	0
Sulfate	SO_4^{-2}	0.016
Chloride	Cl^-	0.11
Oxalate	$(\text{COO})_2^{-2}$	0.00023
Citrate	$\text{C}_3\text{H}_5(\text{COO})_3^{-3}$	0.0026
Urea	$(\text{NH}_2)_2\text{CO}$	0.27
pH		6.2

It was noted in Chapter 2 that the hydrolysis of urea in urine collections systems results in the release of ammonium and carbonate ions (see Equation 2.1), causing an increase in pH. An Excel spreadsheet was used to calculate the equilibrium pH of urine as a function of various degrees of urea hydrolysis. Additionally, the corresponding degree of oversaturation with respect to various mineral phases was calculated. The flow sheet illustrating the sequence of these calculations is shown in Figure 3.1.

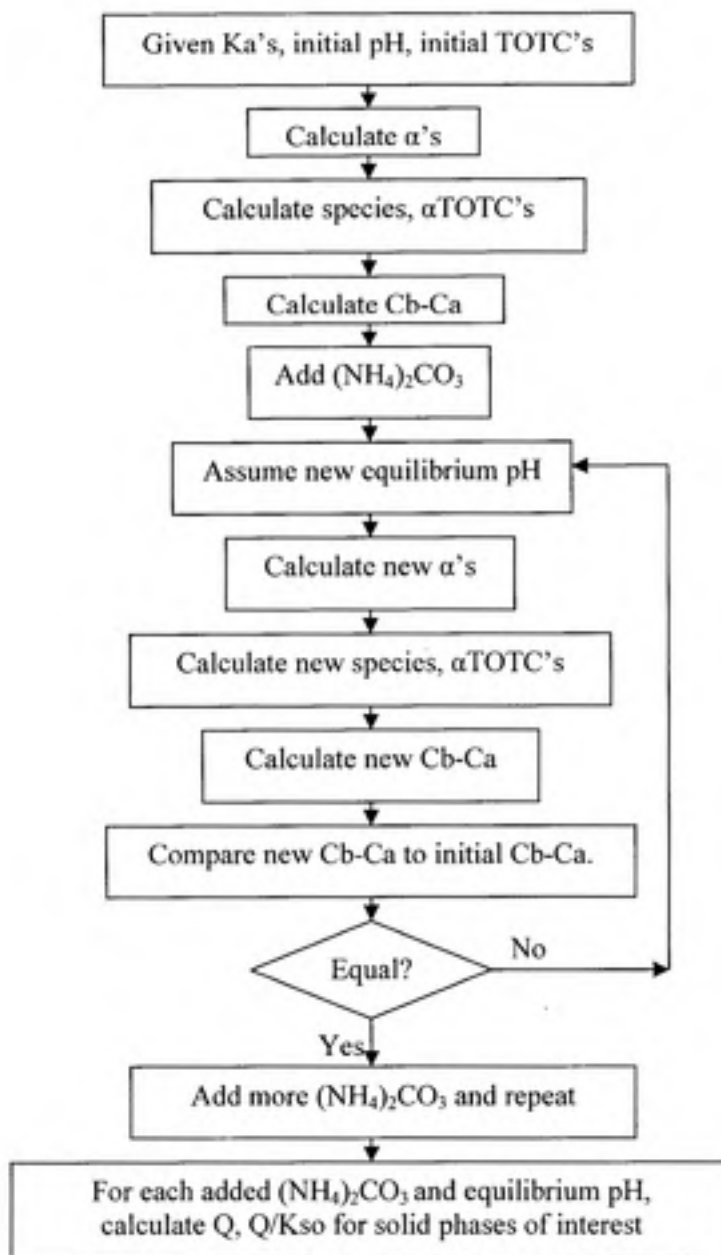


Figure 3.1 Flow diagram illustrating equilibrium pH and precipitation potential calculations

In order to generate the equilibrium pH for varying degrees of urea hydrolysis, it was necessary to first find the concentrations of other cations and anions present in the system so that the charge balance, or electroneutrality condition, would be satisfied. Equation 3.1 is the charge balance equation, rearranged to represent the acid neutralizing capacity of the system (Cb-Ca), where Cb-Ca denotes the concentration of strong base

cations minus the concentration of strong acid anions. In developing Equation 3.1, it is assumed that the ammonium ion, and carbonate (CO_3^{2-}), phosphate (PO_4^{3-}), oxalate (Ox^{2-}) and citrate (Cit^{3-}) species are the only proton donors and acceptors in the system, other than H^+ and OH^- .

$$\begin{aligned} Cb - Ca = & [\text{OH}^-] - [\text{H}^+] - [\text{NH}_4^+] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] \\ & + [\text{HOx}^-] + 2[\text{Ox}^{2-}] + [\text{H}_2\text{PO}_4^-] + 2[\text{HPO}_4^{2-}] + 3[\text{PO}_4^{3-}] \\ & + [\text{H}_2\text{Cit}^-] + 2[\text{HCit}^{2-}] + 3[\text{Cit}^{3-}] \end{aligned} \quad (3.1)$$

Equation 3.1 can be rewritten as

$$\begin{aligned} Cb - Ca = & [\text{OH}^-] - [\text{H}^+] - \alpha_0 \text{TOTNH}_3 + \alpha_1 \text{TOTCO}_3 + 2\alpha_2 \text{TOTCO}_3 \\ & + \alpha_1 \text{TOTOx} + 2\alpha_2 \text{TOTOx} + \alpha_1 \text{TOTPO}_4 + 2\alpha_2 \text{TOTPO}_4 + 3\alpha_3 \text{TOTPO}_4 \\ & + \alpha_1 \text{TOTCit} + 2\alpha_2 \text{TOTCit} + 3\alpha_3 \text{TOTCit} \end{aligned} \quad (3.2)$$

where TOTNH_3 , TOTCO_3 , TOTOx , TOTPO_4 , and TOTCit are the total concentrations of ammonia, carbonate, oxalate, phosphoric acid, and citrate and the alpha values represent distribution coefficients that describe the speciation of the different acids and bases in the system in accordance with the following illustrative equations:

a) for ammonia

$$\alpha_0 = \frac{[\text{NH}_4^+]}{\text{TotNH}_3} = \frac{[\text{H}^+]}{(K_{a1} + [\text{H}^+])} \quad (3.3)$$

b) for carbonate

$$\alpha_0 = \frac{[\text{H}_2\text{CO}_3]}{\text{TotCO}_3} = \frac{[\text{H}^+]^2}{([\text{H}^+]^2 + K_{a1}[\text{H}^+] + K_{a1}K_{a2})} \quad (3.4)$$

$$\alpha_1 = \frac{[\text{HCO}_3^-]}{\text{TotCO}_3} = \frac{K_{a1}[\text{H}^+]}{([\text{H}^+]^2 + K_{a1}[\text{H}^+] + K_{a1}K_{a2})} \quad (3.5)$$

$$\alpha_2 = \frac{[CO_3^{-2}]}{TotCO_3} = \frac{K_{a1}K_{a2}}{([H+]^2 + K_{a1}[H^+] + K_{a1}K_{a2})} \quad (3.6)$$

c) for phosphate

$$\alpha_0 = \frac{[H_3PO_4]}{TotPO_4} = \frac{[H^+]^3}{([H+]^3 + K_{a1}[H^+]^2 + K_{a1}K_{a2}[H^+] + K_{a1}K_{a2}K_{a3})} \quad (3.7)$$

$$\alpha_1 = \frac{[H_2PO_4^-]}{TotPO_4} = \frac{K_{a1}[H^+]^2}{([H+]^3 + K_{a1}[H^+]^2 + K_{a1}K_{a2}[H^+] + K_{a1}K_{a2}K_{a3})} \quad (3.8)$$

$$\alpha_2 = \frac{[HPO_4^{-2}]}{TotPO_4} = \frac{K_{a1}K_{a2}[H^+]}{([H+]^3 + K_{a1}[H^+]^2 + K_{a1}K_{a2}[H^+] + K_{a1}K_{a2}K_{a3})} \quad (3.9)$$

$$\alpha_3 = \frac{[PO_4^{-3}]}{TotPO_4} = \frac{K_{a1}K_{a2}K_{a3}}{([H+]^3 + K_{a1}[H^+]^2 + K_{a1}K_{a2}[H^+] + K_{a1}K_{a2}K_{a3})} \quad (3.10)$$

Distribution coefficients for oxalate and citrate are similarly defined.

Given the initial pH of the system (6.2), the acidity constants (Table 3.3) for the ammonium ion, carbonic acid, phosphoric acid, oxalic acid, and citric acid, and the initial total concentrations of ammonia (TOTNH₄), carbonate (TOTCO₃), oxalate (TOTOx), Citrate (TOTCit), and phosphate (TOTPO₄), the initial acid neutralizing capacity for the system can be calculated using Equation 3.2 before any urea hydrolysis occurs.

Table 3.3 Equilibrium constants for acidic species present in urine (from Benjamin 2002)

Name	Formula	pK _{a1} [†]	pK _{a2} [†]	pK _{a3} [†]
Ammonium ion	NH ₄ ⁺	9.25		
Carbonic acid	H ₂ CO ₃	6.35	10.33	
Oxalic acid	(COOH) ₂	0.9	4.2	
Citric acid	C ₃ H ₄ OH(COOH) ₃	3.13	4.72	6.33
Phosphoric Acid	H ₃ PO ₄	2.16	7.2	12.35

[†]pKa represents the negative log of the acidity constant

Once the acid neutralizing capacity of the system was determined, the hydrolysis of urea ($(\text{NH}_2)_2\text{CO}$) was simulated by essentially titrating the urine with ammonium carbonate $(\text{NH}_4)_2\text{CO}_3$. For each addition of $(\text{NH}_4)_2\text{CO}_3$, a new pH was assumed and αTOTC values for each species in Equation 3.2 were calculated. The TOTC values for ammonium and carbonate shown in Table 3.2 were increased by the amount of ammonium and carbonate added as a result of the hydrolysis of urea (Equation 2.1). The other species in Table 3.2 remained constant. Using the assumed pH and the newly calculated αTOTC values for each solute, a new acid neutralizing capacity (Cb-Ca) was determined using Equation 3.2. If this new Cb-Ca value was not equal to the original acid neutralizing capacity, then a new pH was assumed and the Cb-Ca value was recalculated. This process was repeated until the calculated Cb-Ca value was consistent with the original value. The pH at which this equality was achieved represented the equilibrium pH for that increment of urea hydrolyzed. The calculations were repeated for different degrees of urea hydrolysis.

To predict the precipitation potential for various mineral deposits associated with the hydrolysis of urea, the degree of oversaturation with respect to six mineral phases was considered: calcite, dicalcium phosphate anhydride (DCPA), dicalcium phosphate dihydrate (DCPD), calcium hydroxylapatite (HAP), octacalcium phosphate (OCP), and struvite (magnesium ammonium phosphate). These mineral phases were chosen because they are either found to occur in urine-collecting systems, or are known to precipitate from natural solutions containing calcium and phosphate (Udert 2003b). The elemental composition and solubility product (pK_{so}) for each solid is found in Table 3.4.

Table 3.4 Solubility constants for selected solids (source: Udert et al, 2003b)

Chemical Name	Mineral Name or Abbreviation	Chemical Formula	pK _{so} [†] at Ionic Strength = 0
Calcium Carbonate	Calcite	CaCO ₃	8.48
Dicalcium Phosphate Anhydride	DCPA	Ca(HPO ₄)	6.9
Dicalcium Phosphate Dihydrate	DCPD	Ca(HPO ₄)-2H ₂ O	6.6
Calcium Hydroxylapatite	HAP	Ca ₅ (PO ₄) ₃ (OH)	57.5
Octacalcium Phosphate	OCP	Ca ₈ H ₂ (PO ₄) ₆ (OH) ₂ -5H ₂ O	48.4
Magnesium Ammonium Phosphate	Struvite	MgNH ₄ PO ₄ -6H ₂ O	13.15

†pK_{so} represents the negative log of the solubility product, K_{so}

For each of the six solids, the reaction quotient, Q, was calculated for each incremental degree of urea hydrolysis. The reaction quotient for a solid is the product of the concentrations of the components of that solid. An example is the reaction quotient for struvite:

$$Q = [Mg^{+2}][NH_4^+][PO_4^{-3}] = [Mg^{+2}](\alpha_0 TOTNH_3)(\alpha_3 TOTPO_4) \quad (3.11)$$

The degree of oversaturation for each solid was calculated as the reaction quotient divided by the solubility product (Q/K_{so}).

All calculations described up to this point were performed assuming an ionic strength (IS) of zero. Given the relatively high ionic strength of urine, the calculations were adjusted to account for activity effects. A summary of these calculations is presented in the flow diagram in Figure 3.2.

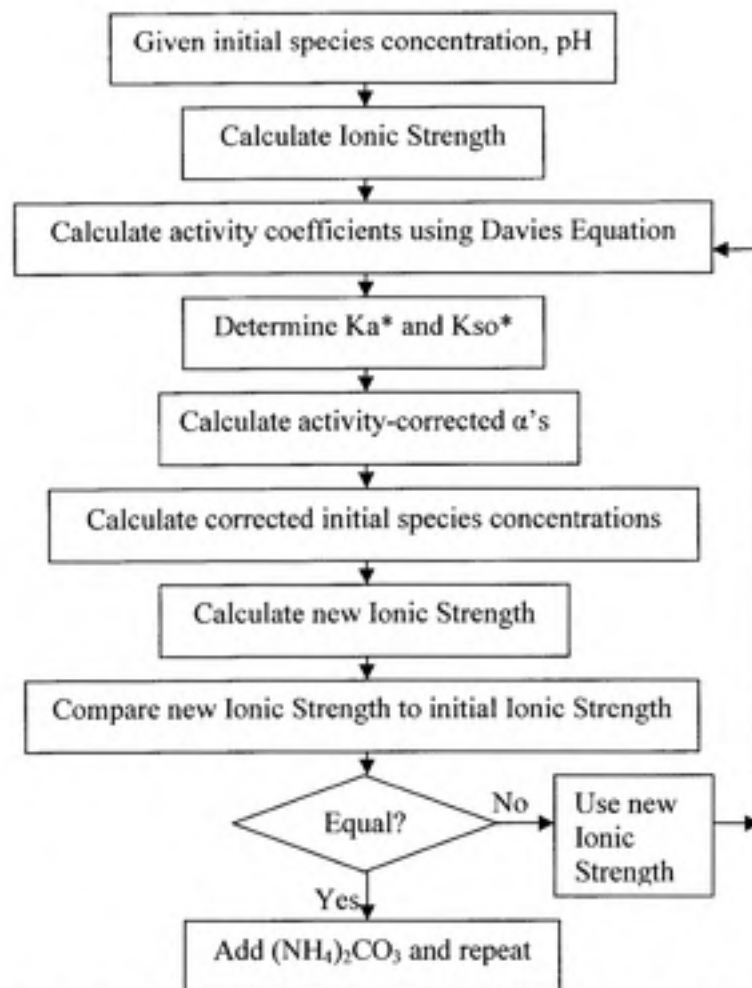


Figure 3.2 Flow diagram showing calculations of ionic strength and activity-adjusted equilibrium constants

The first step in the ionic strength calculations was to use an iterative process to determine the initial ionic strength of the system. This was done by first assuming an ionic strength value of zero and the thermodynamic equilibrium constants given in Table 3.3. The new ionic strength was then calculated using the alpha values and the total species concentrations using Equation 3.12

$$I = \frac{1}{2} \sum_{i=1}^n c_i z_i^2 \quad (3.12)$$

where c represents the concentration of each species and z is the charge of that species. The concentrations of Na^+ , Ca^{+2} , Mg^{+2} , K^+ , Cl^- , and SO_4^{-2} were included in the calculation of ionic strength.

A second iteration was performed using the newly calculated ionic strength from the first iteration. Activity coefficients for each species were calculated using the Davies Equation:

$$\log f = 0.509z^2 \left[\frac{\sqrt{I}}{(1 + \sqrt{I}) - 0.2I} \right] \quad (3.13)$$

where f is the activity coefficient.

The activity coefficients were used to generate new acidity constants, K_a^* , which are corrected for activity. Examples of this calculation for citrate are shown below.

$$K_{a1}^* = \frac{K_{a1} f_{\text{H}_3\text{Cit}}}{f_{\text{H}_2\text{Cit}^-}} \quad (3.14)$$

$$K_{a2}^* = \frac{K_{a2} f_{\text{H}_2\text{Cit}^-}}{f_{\text{HCit}^{-2}}} \quad (3.15)$$

$$K_{a3}^* = \frac{K_{a3} f_{\text{HCit}^{-2}}}{f_{\text{Cit}^{-3}}} \quad (3.16)$$

These K_a^* values were used to calculate new alpha values, which were in turn used to find the corrected concentration of each species in the system. These corrected concentrations were then used to calculate a new ionic strength. This iteration process

was repeated until the ionic strength found at the end of the iteration was equal to the ionic strength value of the previous iteration. The final ionic strength of the system was found to be 0.239; this value was used to calculate the new Cb-Ca for the equilibrium pH iterations.

This ionic strength was assumed to remain constant throughout the simulated addition of ammonium carbonate. In reality, however, the hydrolysis of urea would cause the ionic strength of the system to increase slightly with each step. In order to check if the use of a constant ionic strength is a reasonable assumption, two alternate simulations were performed. First, assuming that the ionic strength remained constant 0.239, and second, assuming that all of the 0.27 mol/L of urea had been hydrolyzed, a new ionic strength was calculated. While the ionic strength was found to increase as urea is hydrolyzed, use of the higher ionic strength to find the equilibrium pH showed that the final equilibrium pH was not significantly changed using this higher ionic strength. It was therefore determined that a constant ionic strength could be assumed throughout the urea hydrolysis simulation without impacting the calculations.

Activity-corrected solubility constants, K_{so}^* , were calculated using the activity coefficients corresponding to an ionic strength of 0.239. An example calculation is shown in Equation 3.17 for struvite.

$$K_{so}^* = \frac{K_{SO}}{\gamma_{Mg^{+2}} \gamma_{NH_4^+} \gamma_{PO_4^{-3}}} \quad (3.17)$$

These activity-corrected K_{so}^* values were used to calculate the degree of oversaturation for the each of the solid phases of concern.

Chapter 4

Results and Discussion

4.1 Deposits in Drain Pipes Behind Waterless Urinals

All drain pipes which were sampled are summarized in Table 4.1, along with information regarding the deposit collected at some of those locations.

Table 4.1 Summary of sampling locations

	Building Name Sample Name	Urinal System	Facility Usage	Deposit Found	Sample Date	Analysis	Fig
1	Giles Horney-- Conventional	Conventional --flush	Low Usage	None	Sept 2007		4.1
2	Giles Horney-- Water Saving	Falcon-3 yr, Eco-1 yr	Low Usage	Substantial	Sept 2007	XRD, SEM	4.2
3	Energy Services	Eco--1 year	Very Low Usage	None	Sept 2007		4.3
4	Bondurant	Eco--1 year	High Usage	Very little	Sept 2007	XRD	
5	R.B. House	Falcon-3 yr, Eco-1 yr	High Usage	Some	Sept 2007		4.4
6	FedEx Global-- 1st Floor	Falcon--6 months	High Usage	Substantial	Nov 2007	XRD, SEM	4.5
7	FedEx Global-- 1st Floor	Falcon--1.5 years	High Usage	Substantial	Sept 2008	XRD	
8	FedEx Global-- 4th Floor	Falcon--6 months	Very Low Usage	Some	Nov 2007	XRD	
9	RDU airport-- Terminal A	Falcon--6 years	Very High Usage	Substantial	Nov 2007	XRD, SEM	4.6
10	RDU airport-- Operations	Falcon--4 years	Low Usage	Substantial	Nov 2007	XRD	

Photographs taken of the drain pipes behind the waterless urinals are shown in the figures below. The location number given with each photograph corresponds to the first column in Table 4.1. The drain pipe behind the conventional flush urinal showed no deposit only some corrosion of the cast iron pipe (Figure 4.1). A Falcon Waterfree urinal was located adjacent to this urinal; its pipe showed substantial deposit (Figure 4.2). Urinals that had used only an Eco cartridge (e.g. Figure 4.3) showed little to no deposit.

The drain pipes showing the largest amount of deposit (Figures 4.2, 4.5, and 4.6) were in locations where the urinal system used was a Falcon cartridge or in locations where a Falcon cartridge had been used initially.

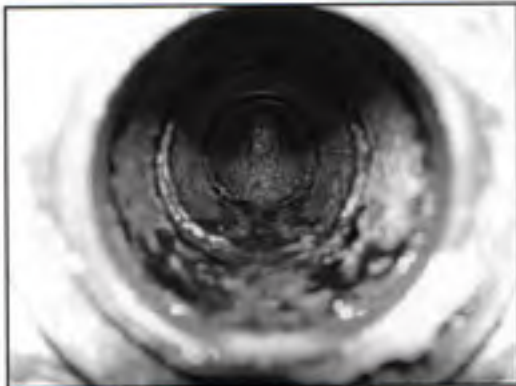


Figure 4.1 Conventional flush urinal, Giles Horney Building (location 1)

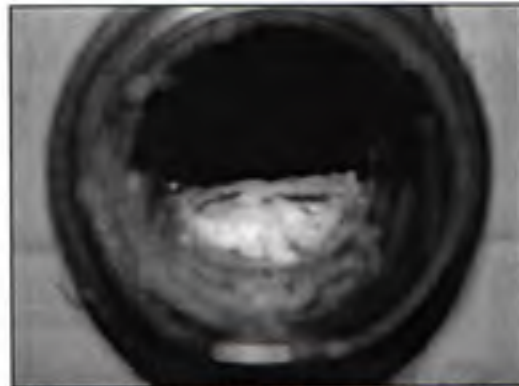


Figure 4.2 Falcon Waterfree urinal, Giles Horney Building (location 2)

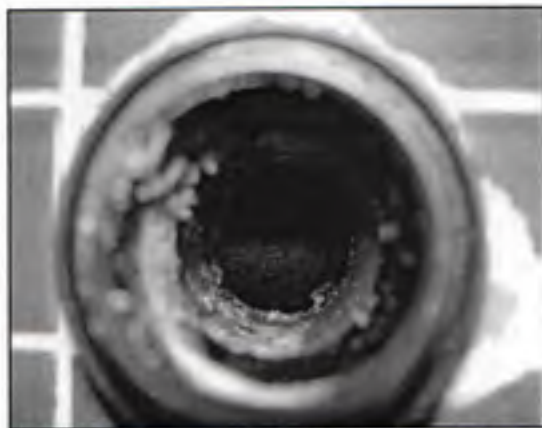


Figure 4.3 Falcon urinal with Eco cartridge, Energy Services Building (location 3)



Figure 4.4 Falcon urinal with Eco cartridge R.B. House Undergraduate Library (location 5)

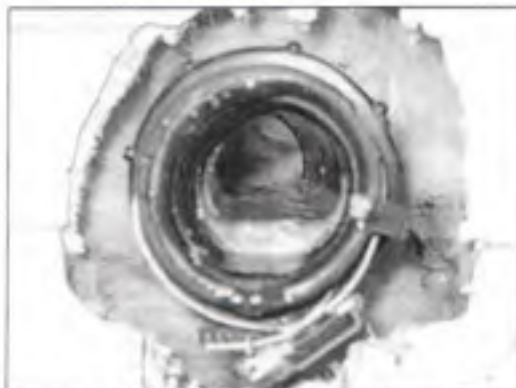


Figure 4.5 Falcon Urinal and cartridge, Fed Ex Global Education 1st floor (location 6)

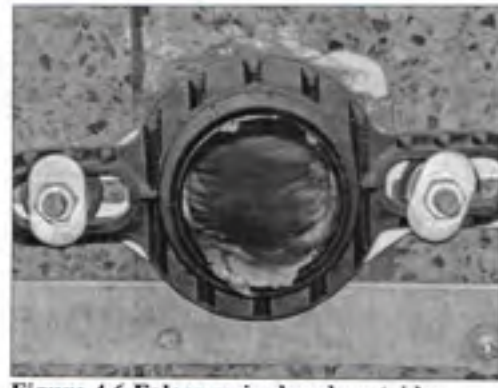


Figure 4.6 Falcon urinal and cartridge, Raleigh Durham Airport, Terminal A (location 9)

4.2 Chemical Equilibrium Modeling

The first calculations generated for the chemical equilibrium model were the distribution coefficients (alpha values). Using the acidity constants (K_a values) from Benjamin (2002) and a pH of 6.2, the species distribution coefficients (alpha values) were calculated using Equations 3.3 through 3.10. Using these alpha values and the total concentrations of the different proton donating and accepting compounds present in urine (see Table 4.2), the acid neutralizing capacity (Cb-Ca) was determined using Equation 3.2. Table 4.3 shows the acidity constants, distribution coefficients, and total concentrations for each acid/base couple of concern, as well as the calculated acid neutralizing capacity of the system. All of these calculations were performed assuming zero ionic strength.

Table 4.2 Major species present in urine (all concentrations in mol/L)

Ammonia	Calcium	Magnesium	Sodium	Potassium	Urea
NH_3	Ca^{+2}	Mg^{+2}	Na^+	K^+	$(\text{NH}_2)_2\text{CO}$
0.034	0.0046	0.0039	0.12	0.056	0.27

Phosphate	Carbonate	Sulphate	Chloride	Oxalate	Citrate
PO_4^{-3}	CO_3^{-2}	SO_4^{-2}	Cl^-	$(\text{COO})_2^{-2}$	$\text{C}_3\text{H}_5(\text{COO})_3^{-3}$
0.024	0	0.016	0.11	0.00023	0.0026

Table 4.3 Summary of acidity constants and distribution coefficients for proton donors and acceptors present in urine

pH=6.2, IS = 0	TOTNH ₄	TOTCO ₃	TOTOx	TOTCit	TOTPO ₄
Ka1	5.62E-10	4.47E-07	1.26E-01	7.41E-04	6.92E-03
Ka2	-	4.68E-11	6.31E-05	1.91E-05	6.31E-08
Ka3	-	-	-	4.68E-07	4.47E-13
alpha0	9.99E-01	5.85E-01	5.01E-06	8.50E-04	9.12E-05
alpha1	8.90E-04	4.14E-01	9.90E-03	1.87E-02	9.09E-01
alpha2	-	3.07E-05	9.90E-01	5.64E-01	9.09E-02
alpha3	-	-	-	4.18E-01	6.44E-08
Conc (mol/L)	3.40E-02	0.00E+00	2.30E-04	2.60E-03	2.40E-02
Cb-Ca =			-0.00110 eq/L		

Because urine is known to have an ionic strength well above zero, calculations were then performed to determine the ionic strength of the system and the associated activity-adjusted equilibrium constants. These calculations are illustrated in Table 4.4. For each species present in the system, column 1 shows the charge squared and column 2 shows the concentration. The concentrations shown in column 2 were calculated by multiplying the alpha value for that species by the total concentration given in Table 4.2. The ionic strength shown at the bottom of Table 4.4 is the summation of all the cz^2 values in column 3 multiplied by 0.5 (see Equation 3.13). Column 4 gives the activity coefficient (f) for each species, calculated using the Davies equation in accordance with Equation 3.14 and the new ionic strength. The activity coefficients in column 4 are then used to calculate a new concentration for each species (column 5). Column 6 presents the calculations for determination of the new ionic strength based on the revised concentrations of each species.

Table 4.4 Calculations to determine ionic strength and activity-adjusted acidity constants

	IS=0 & urea hydrolyzed=0			IS=0.232 & urea hydrolyzed=0		
	(1)	(2)	(3)	(4)	(5)	(6)
	charge ² z ²	conc, c	cz ²	f	conc, c	cz ²
H ₂ PO ₄ ⁻	1	2.18E-02	2.18E-02	0.721	1.89E-02	1.89E-02
HPO ₄ ⁻²	4	2.18E-03	8.73E-03	0.271	5.05E-03	2.03E-02
PO ₄ ⁻³	9	1.54E-09	1.39E-08	0.053	1.83E-08	1.67E-07
H ₃ Cit	0	2.21E-06	0.00E+00	1		0.00E+00
H ₂ Cit ⁻	1	4.85E-05	4.85E-05	0.721	6.71E-06	6.62E-06
HCit ⁻²	4	1.47E-03	5.86E-03	0.271	5.40E-04	2.14E-03
Cit ⁻³	9	1.09E-03	9.78E-03	0.053	2.05E-03	1.85E-02
H ₂ Ox	0	1.15E-09	0.00E+00	1		0.00E+00
HOx ⁻	1	2.28E-06	2.28E-06	0.721	8.60E-07	8.54E-07
Ox ⁻²	4	2.28E-04	9.11E-04	0.271	2.29E-04	9.17E-04
H ₂ CO ₃	0	0.00E+00	0.00E+00	1		0.00E+00
HCO ₃ ⁻	1	0.00E+00	0.00E+00	1	0.00E+00	0.00E+00
CO ₃ ⁻²	4	0.00E+00	0.00E+00	0	0.00E+00	0.00E+00
NH ₄ ⁺	1	3.40E-02	3.40E-02	0.721	3.40E-02	3.40E-02
NH ₃	0	3.03E-05	0.00E+00	1	4.20E-05	0.00E+00
Mg ⁺²	4	3.90E-03	1.56E-02	0.271	3.90E-03	1.56E-02
Ca ⁺²	4	4.60E-03	1.84E-02	0.271	4.60E-03	1.84E-02
OH ⁻	1	0.00E+00	0.00E+00	0.721		0.00E+00
H ⁺	1	0.00E+00	0.00E+00	0.721		0.00E+00
Na ⁺	1	1.20E-01	1.20E-01	0.721	1.20E-01	1.20E-01
K ⁺	1	5.60E-02	5.60E-02	0.721	5.60E-02	5.60E-02
Cl ⁻	1	1.10E-01	1.10E-01	0.721	1.10E-01	1.10E-01
SO ₄ ⁻²	4	1.60E-02	6.40E-02	0.271	1.60E-02	6.40E-02
IONIC STRENGTH			0.233			0.239

Only the first iteration is detailed in Table 4.4; a summary of all the iterations is shown in Table 4.5. In the 4th iteration, it is seen that the ionic strength converges to a constant value. This value (0.239) represents the initial ionic strength of the system, before any urea hydrolysis occurs.

Table 4.5 Summary of the iterative process used to determine initial ionic strength

Iteration Number	1	2	3	4
Ionic Strength	0.00E+00	2.33E-01	2.39E-01	2.39E-01
Amt Urea Hydrolyzed	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Cb-Ca, eq/L	-1.10E-03	2.80E-03	2.83E-03	2.83E-03
New Ionic Strength	2.33E-01	2.39E-01	2.39E-01	2.39E-01

Using $I=0.239$ as the ionic strength of the system, the final activity-adjusted acidity constants and distribution coefficients were calculated using the process described in Chapter 3. These final activity-adjusted values, and the corresponding acid neutralizing capacity, are shown in Table 4.6.

Table 4.6 Summary of activity-adjusted acidity constants and distribution coefficients

pH=6.2, IS = 0.239	TOTNH ₄	TOTCO ₃	TOTOx	TOTCit	TOTPO ₄
Ka1*	7.81E-10	6.21E-07	1.75E-01	1.03E-03	9.61E-03
Ka2*	-	1.25E-10	1.69E-04	5.11E-05	1.69E-07
Ka3*	-	-	-	2.42E-06	2.31E-12
alpha0	9.99E-01				
alpha1	1.24E-03	4.96E-01	3.71E-03	2.54E-03	7.88E-01
alpha2	-	9.86E-05	9.96E-01	2.06E-01	2.11E-01
alpha3	-	-	-	7.91E-01	7.75E-07
Conc (mol/L)	3.40E-02	0.00E+00	2.30E-04	2.60E-03	2.40E-02
Cb-Ca =		0.00283 eq/L			

The simulation of urca hydrolysis, equivalent to a titration of the urine with ammonium carbonate, was then performed. Examples of some of the calculations are shown in Table 4.7. The two input values are shown in columns 1 and 4. As ammonium carbonate ($(\text{NH}_4)_2\text{CO}_3$) is added in small increments, corresponding to various degrees of urea hydrolysis, all other columns are calculated using Excel. Column 2 begins at 0.034 mol/L which is the initial ammonia concentration in the system prior to any urea hydrolysis; the ammonia concentration increases as $(\text{NH}_4)_2\text{CO}_3$ is added to the system. Column 3 starts at 0 because there is no carbonate initially, and increases as $(\text{NH}_4)_2\text{CO}_3$ is added. To run the model, an initial pH must be assumed as shown in column 4. Columns 5, 6, 8, 9, 11, 12, 14-16, and 18-20 show the distribution coefficients calculated using Equations 3.4 to 3.11. Input information for these calculations is the H^+ concentration calculated from pH and the respective activity-adjusted acidity constants. The acid neutralizing capacity (column 22) is determined by using the entries in columns 7, 10, 13, 17, and 21, along with $[\text{OH}^-]$ and $[\text{H}^+]$, in accordance with Equation 3.2. If the value generated in column 22 was not equal to the actual acid neutralizing capacity of the system (0.00283 eq/L, as shown in Table 4.6), a new pH was assumed. For each increment of ammonium carbonate added, the pH in column 4 was continually adjusted until the value in column 22 was equal to 0.00283 eq/L. This process was repeated for various additions of ammonium carbonate to complete the titration.

Table 4.7 Urea hydrolysis sample calculations

(1)	(2)	(3)	(4)	Ammonia			Carbonate		
				(5)	(6)	(7)	(8)	(9)	(10)
Amt (NH ₄) ₂ CO ₃ added	TOT NH ₄	TOT CO ₃	pH	α ₀	α ₁	α ₀ *TOT NH ₄	α ₁	α ₂	(α ₁ +2α ₂)* TOTCO ₃
(mol/L)	(mol/L)	(mol/L)					(mol/L)		
0	0.0340	0.0000	6.20	0.999	0.001	0.0340	0.496	0.000	0.00E+00
0.01	0.0540	0.0100	7.03	0.992	0.008	0.0536	0.868	0.001	8.71E-03
0.02	0.0740	0.0200	7.76	0.957	0.043	0.0708	0.966	0.007	1.96E-02
0.03	0.0940	0.0300	8.23	0.883	0.117	0.0830	0.970	0.021	3.03E-02
0.04	0.1140	0.0400	8.43	0.825	0.175	0.0941	0.962	0.033	4.11E-02

Table 4.7 (continued)

Oxalate			Citrate				Phosphate				(22)	
(11)	(12)	(13)	(14)	(15)	(16)	(17)	(18)	(19)	(20)	(21)		
α ₁	α ₂	(α ₁ +2α ₂)* TOTOx	α ₁	α ₂	α ₃	(α ₁ +2α ₂ +3α ₃)* TOTCit	α ₁	α ₂	α ₃	(α ₁ +2α ₂ +3α ₃)* TOTPO ₄	Cb-Ca	
		(mol/L)					(mol/L)				(mol/L)	eq/L
3.71E-03	0.996	4.59E-04	2.54E-03	0.206	0.791	0.00725	0.788	0.211	7.75E-07	0.0291	0.0028	
5.51E-04	0.999	4.60E-04	6.77E-05	0.037	0.963	0.00770	0.355	0.645	1.60E-05	0.0395	0.0028	
1.03E-04	1	4.60E-04	2.42E-06	0.007	0.993	0.00778	0.093	0.907	1.21E-04	0.0458	0.0028	
3.48E-05	1	4.60E-04	2.79E-07	0.002	0.998	0.00779	0.034	0.966	3.79E-04	0.0472	0.0028	
2.18E-05	1	4.60E-04	1.10E-07	0.002	0.998	0.00780	0.021	0.978	6.13E-04	0.0475	0.0028	

Figure 4.7 is a plot of the resulting equilibrium pH as a function of ammonium carbonate added (urea hydrolyzed). As the added amount of ammonium carbonate increases, the equilibrium pH also increases. Note that, for the calculations described above, ionic strength was kept constant at 0.239. As explained in Section 3.3, it is recognized that the addition of (NH₄)₂CO₃ will cause the ionic strength to increase. In the calculations above, it was assumed that the ionic strength was sufficiently high such that the increase in ionic strength due to urea hydrolysis would not significantly affect the final equilibrium pH of the system. To test this assumption, a parallel set of calculations was performed with an ionic strength at 0.392, which assumes that 0.27 M (100%) of the urea in the system has been hydrolyzed (see Table 4.2). It is clear from Figure 4.7 that the

ionic strength change due to the complete hydrolysis of urea does not significantly affect the equilibrium pH of the system.

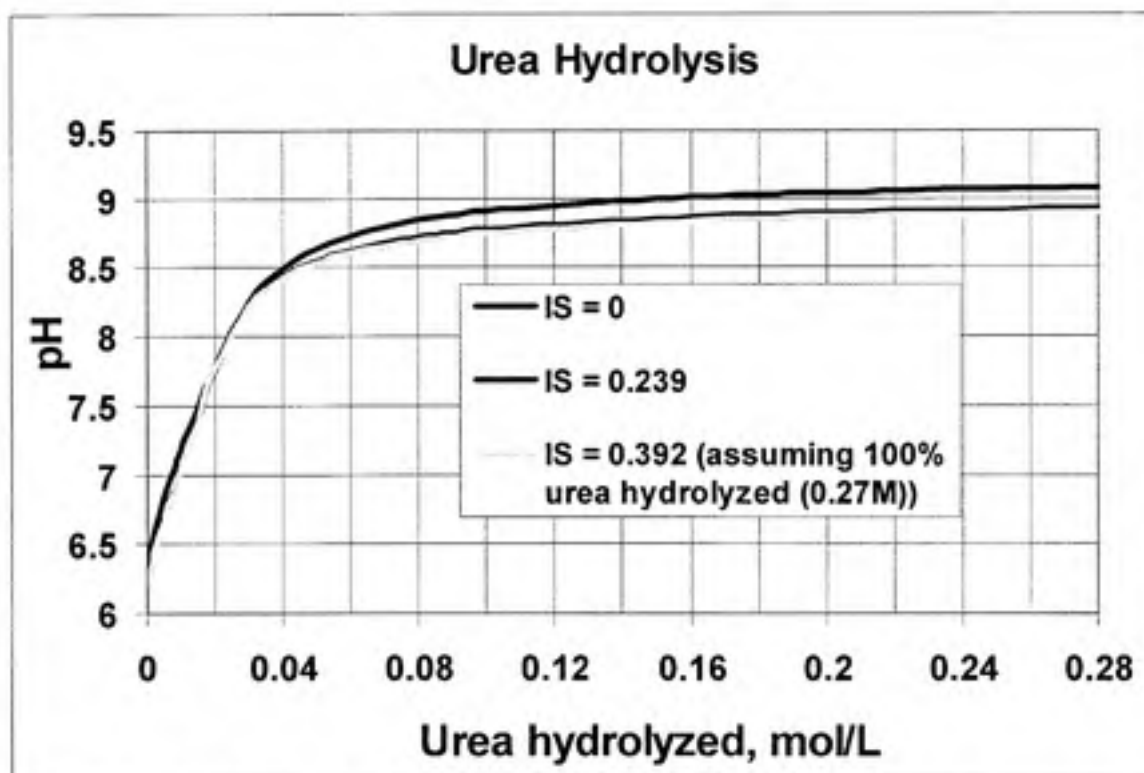


Figure 4.7 Change in equilibrium pH accompanying urea hydrolysis

According to Udert et al (2003b), struvite, calcite and calcium hydroxylapatite are the most common precipitates identified in urine collection systems. Calculations were performed to determine the level of oversaturation with respect to these three minerals in the system. A summary of these calculations is presented in Table 4.8. The amount of ammonium carbonate added (column 1) and the equilibrium pH (column 2) were taken from Table 4.7. The reaction quotients, Q (see Equation 3.12), for each mineral are shown in columns 3, 5, and 7. The K_{so}^* values shown in Table 4.8 are the activity-adjusted solubility products for each of the minerals, calculated in accordance with Equation 3.18. The reaction quotients and K_{so}^* values were used to calculate the degrees

of oversaturation, shown in columns 4, 6, and 8. All of these values are positive, indicating that urine tends to be oversaturated with respect to these three minerals and that the degree of oversaturation increases with the extent of urea hydrolysis. The degrees of oversaturation with respect to calcium hydroxylapatite, struvite, and calcite are shown in Figure 4.8. The degree of oversaturation for these minerals suggests that they are likely to precipitate in the drain pipes behind urinals if there is no water applied to flush the standing urine away.

Table 4.8 Oversaturation of different minerals using activity-adjusted solubility constants at ionic strength = 0.239

(1)	(2)	STRUVITE		CALCITE		HAP**	
		Kso* = 7.08E-16†		Kso* = 2.38E-10†		Kso* = 4.4E-65†	
Amt (NH ₄) ₂ CO ₃ Hydrolyzed (M)	Equilibrium pH	Q=[Mg] [NH ₄][PO ₄]	log (Q/Kso*)	Q= [Ca][CO ₃]	log (Q/Kso*)	Q=[Ca] ⁵ [PO ₄] ³ [OH]	log (Q/Kso*)
0	6.2	2.46E-12	(0.46)	0.00E+00	-	2.10E-43	8.0
0.005	6.69	2.07E-11	0.47	1.05E-08	(0.64)	1.77E-40	10.9
0.01	7.03	8.01E-11	1.05	5.37E-08	0.07	1.24E-38	12.7
0.02	7.76	8.00E-10	2.05	6.42E-07	1.14	2.88E-35	16.1
0.03	8.23	2.95E-09	2.62	2.85E-06	1.79	2.64E-33	18.1
0.04	8.43	5.40E-09	2.88	6.02E-06	2.12	1.78E-32	18.9
0.05	8.55	7.89E-09	3.05	9.72E-06	2.32	5.21E-32	19.4
0.06	8.62	1.04E-08	3.17	1.38E-05	2.48	1.05E-31	19.7
0.08	8.72	1.54E-08	3.34	2.25E-05	2.69	2.51E-31	20.0
0.09	8.75	1.78E-08	3.40	2.71E-05	2.77	3.34E-31	20.2
0.1	8.77	2.03E-08	3.46	3.18E-05	2.84	4.21E-31	20.3

** HAP = Calcium Hydroxylapatite

† Kso* are activity adjusted solubility products

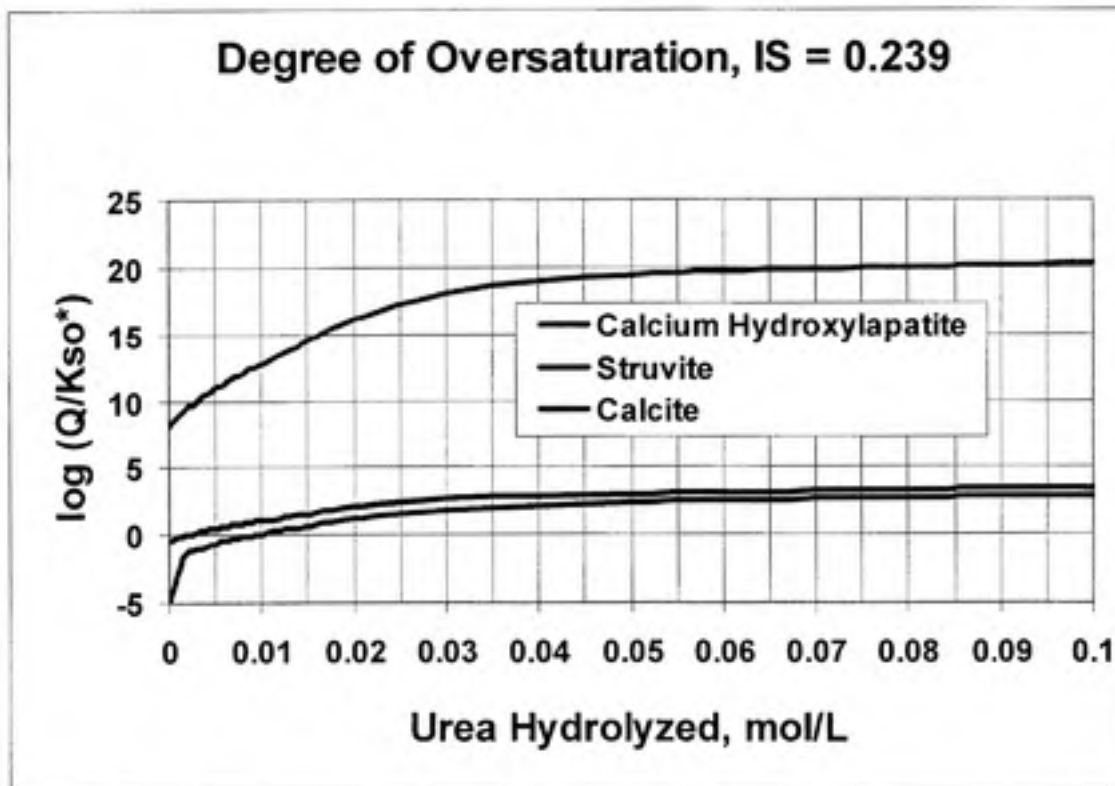


Figure 4.8 Degree of oversaturation with respect to different minerals

4.3 XRD Results

Figures 4.9 and 4.10 show the X-ray diffraction patterns for two of the samples collected. Although one urinal was located on the UNC campus and the other at Raleigh Durham International Airport, the peaks appear to be the same, indicating that the deposit collected from the two locations had the same composition.

Figure 4.11 shows superimposed XRD results for deposits from six of the sampling locations. It is clear from the positions of the major peaks that the composition of the deposits collected is essentially the same, regardless of location. An initial analysis of these XRD patterns in the UNC database showed no match for the major peaks.

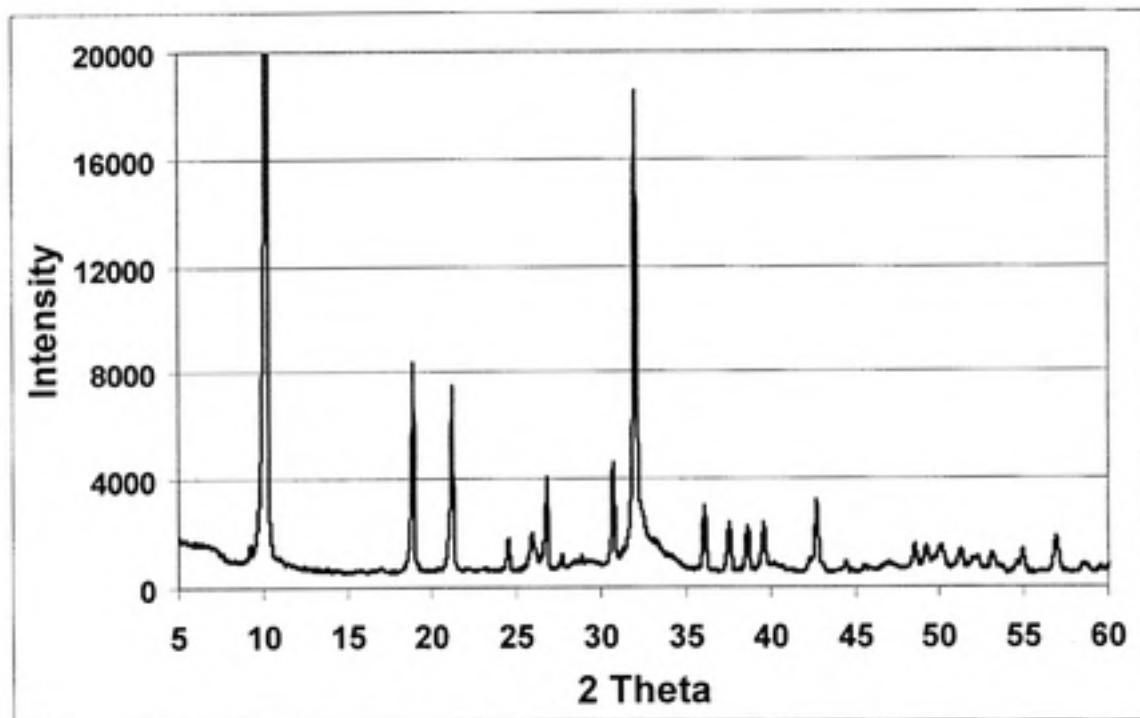


Figure 4.9 X-ray diffraction pattern for sample collected at Giles Horney (location 2)

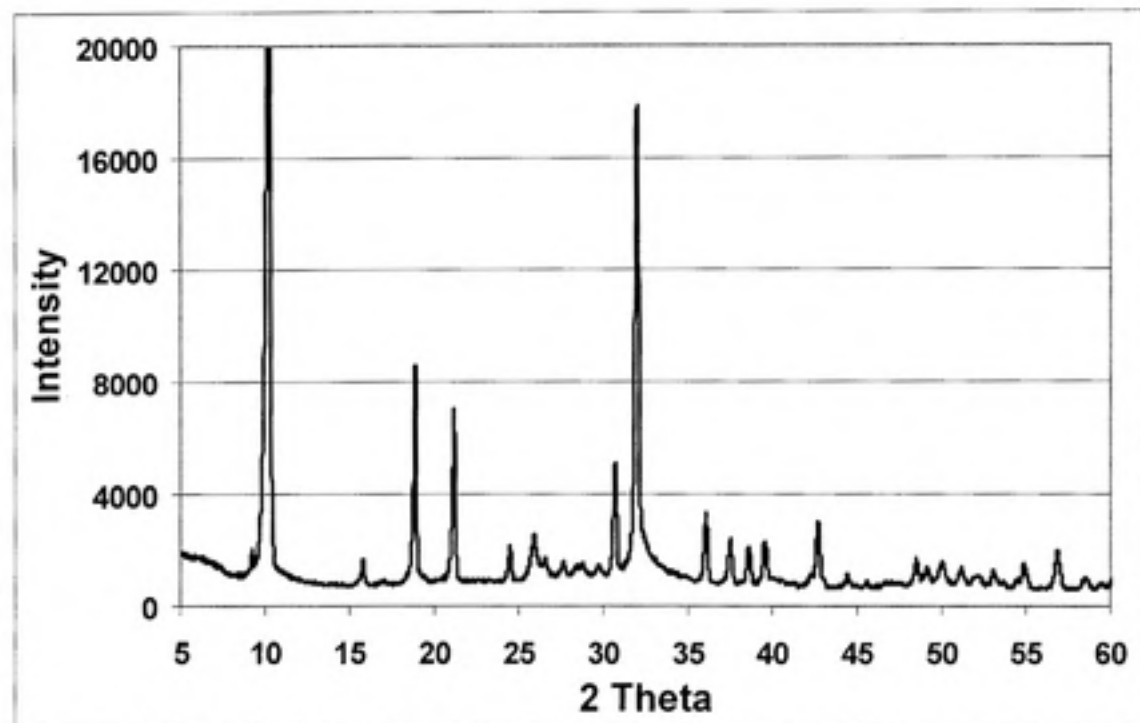


Figure 4.10 X-ray diffraction pattern, RDU airport Terminal A (location 9)

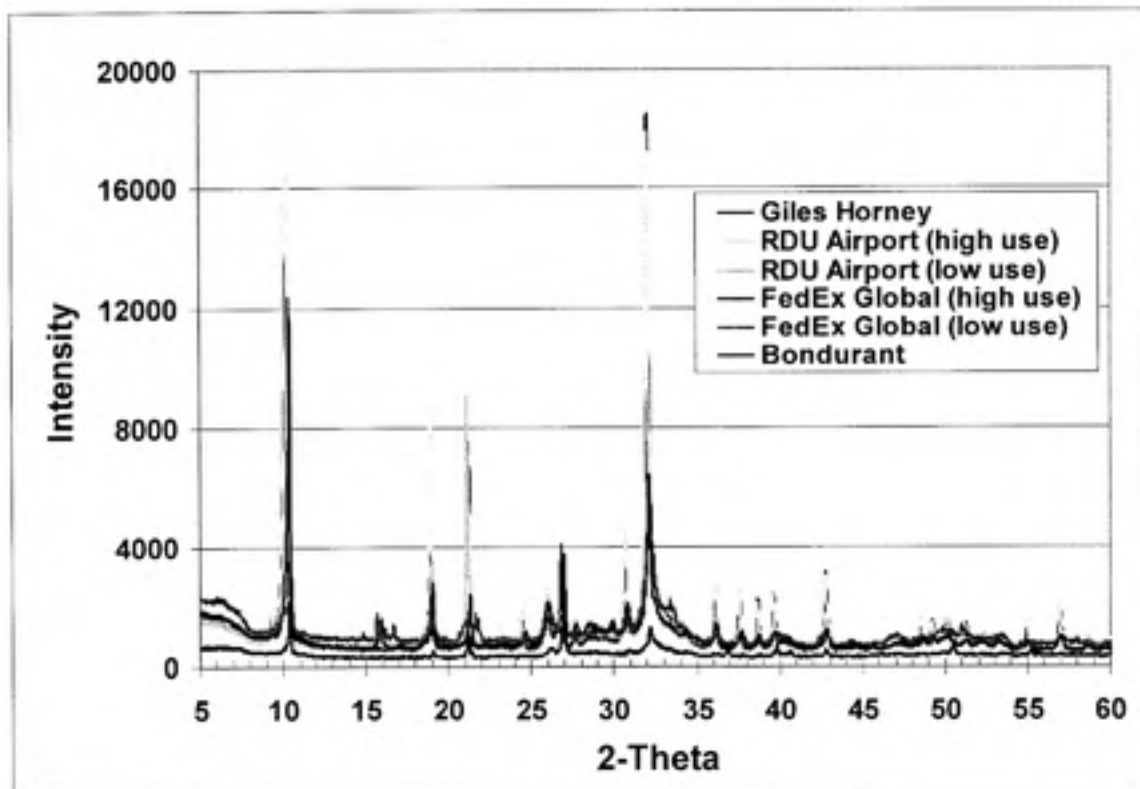


Figure 4.11 X-ray diffraction patterns for six of the samples collected

Because the deposits collected were not successfully identified during the original XRD analysis at UNC, the samples were sent to Dr. Kirk Scheckel of the US Environmental Protection Agency (EPA) in Cincinnati, OH to undergo further analysis. Deposits taken from three different locations (Giles Horney, FedEx Global Education, and RDU Terminal A) were sent to the EPA. The resulting XRD patterns are shown in Figure 4.12. The major peaks line up for all three samples, indicating that they are all of the same composition.

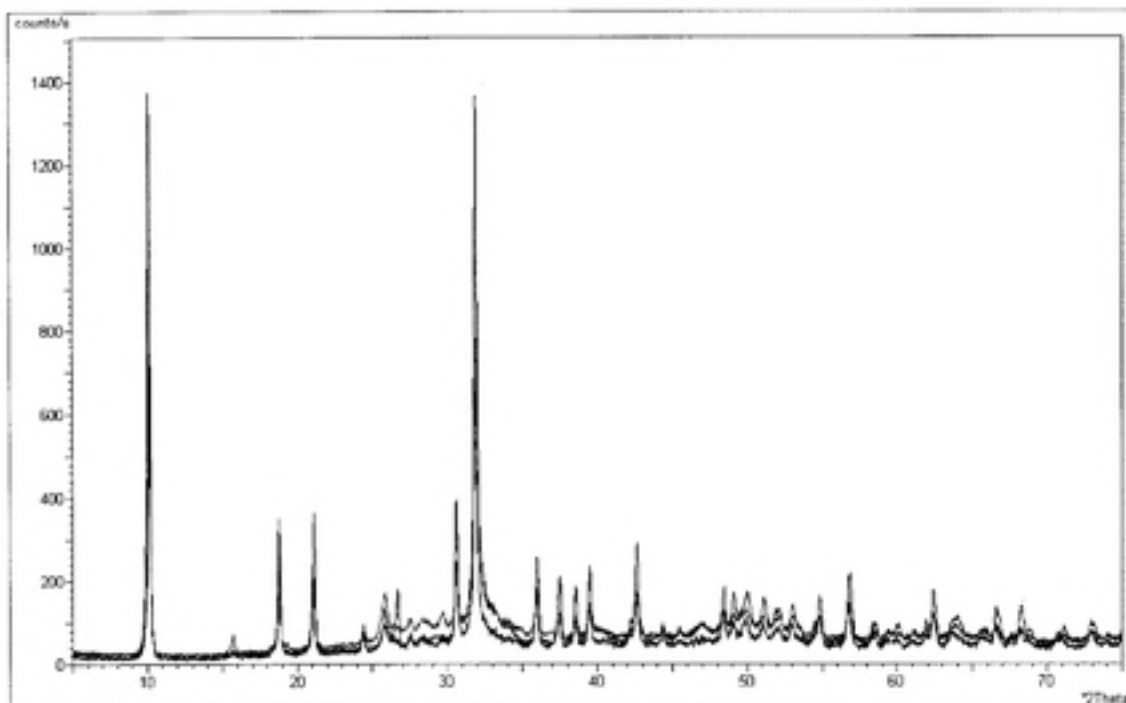


Figure 4.12 XRD patterns for Giles Horney, FedEx Global Education 1st floor, and RDU Terminal A

The EPA laboratory database identified the samples as dittmarite, ($\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$), the monohydrate of struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$). Figure 4.13 shows the diffraction pattern for one of the three samples along with the reference pattern for dittmarite. Like struvite, dittmarite is a mineral form of magnesium ammonium phosphate. However, dittmarite has only one water of hydration.

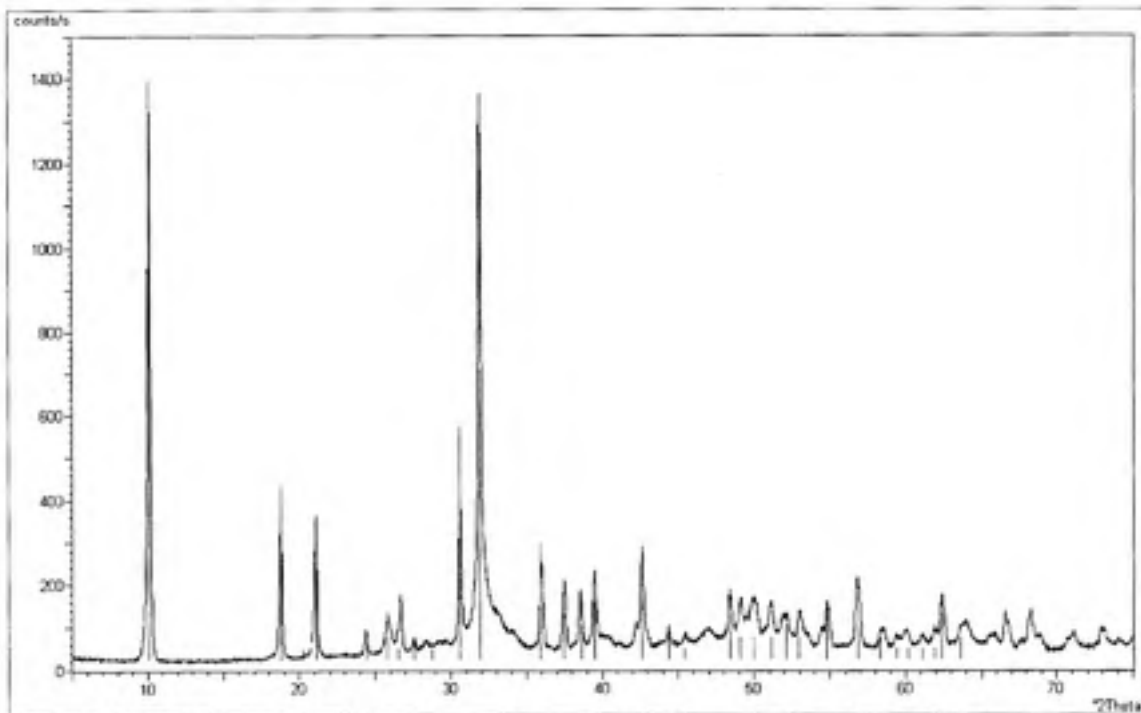


Figure 4.13 XRD Patterns for Giles Horney Sample with Dittmarite ($\text{NH}_4\text{MgPO}_4 \cdot \text{H}_2\text{O}$) reference pattern (20-0663)

Because dittmarite is very similar to the expected mineral struvite, it was believed that the sample was originally struvite but was transformed to dittmarite during processing. According to Bhuiyan et al. (2007) and Sarkar (1991), when struvite is boiled in excess water, it is completely converted to its monohydrate, dittmarite. Because all of the mineral deposits collected from the drain pipes behind the urinals had been sterilized, by autoclaving at 121°C for 18 minutes (see Section 3.2), it is possible that they were transformed to dittmarite during this process.

To test this hypothesis, an additional urinal was removed from one of the restroom walls in the FedEx Global Education building. The deposit from the drain pipe behind this urinal was split into three parts, and each was processed differently. The first portion underwent no processing; it was sent in a 5 mL glass vial to EPA for XRD

analysis in the same form as it had been collected. The second portion was not autoclaved or oven-dried; instead it was air-dried, and ground into a powder. The third portion was processed in an identical manner to the previous samples that had been identified as dittmarite: it was autoclaved, oven-dried, and then ground into a powder. The three samples were sent to the EPA lab for analysis. Figures 4.14 and 4.15 show that samples one and two are identical in composition, while sample three is a different mineral.

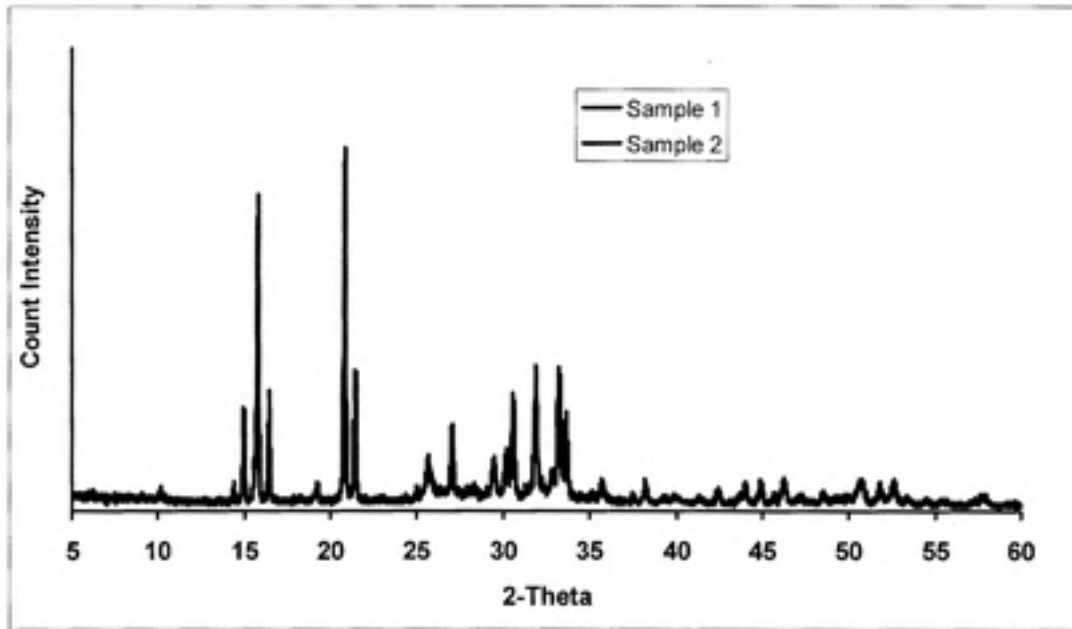


Figure 4.14 XRD Patterns for FedEx Global Education Building samples, not autoclaved or oven-dried

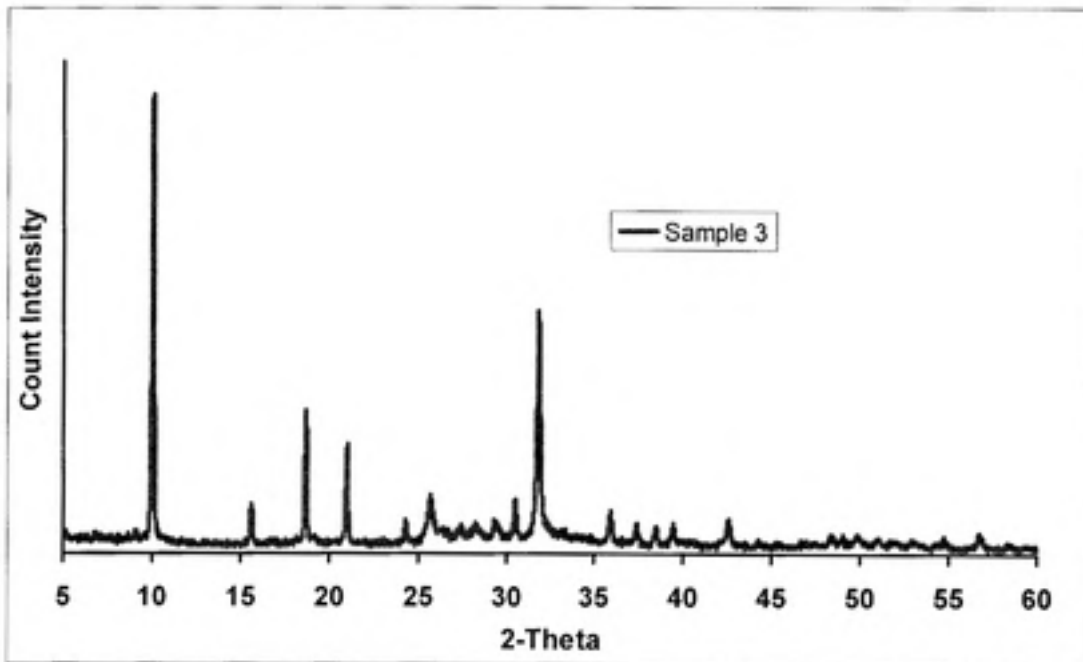


Figure 4.15 XRD Patterns for FedEx Global Education Building sample, autoclaved and oven-dried before XRD analysis

The XRD pattern for each sample was compared with the reference patterns in EPA's library database. It was found that samples 1 and 2 (neither of which was

autoclaved or oven-dried) matched up with the reference peaks for struvite, as shown in Figure 4.16. Sample 3, which had been processed like the original samples (autoclaved and oven-dried) was found to match the reference peaks for dittmarite (Figure 4.17). These results confirm that the mineral deposits found in the drain pipes behind the Waterfree urinals on the UNC campus and at RDU Airport were struvite, and that the sterilization process of autoclaving transformed struvite to dittmarite.

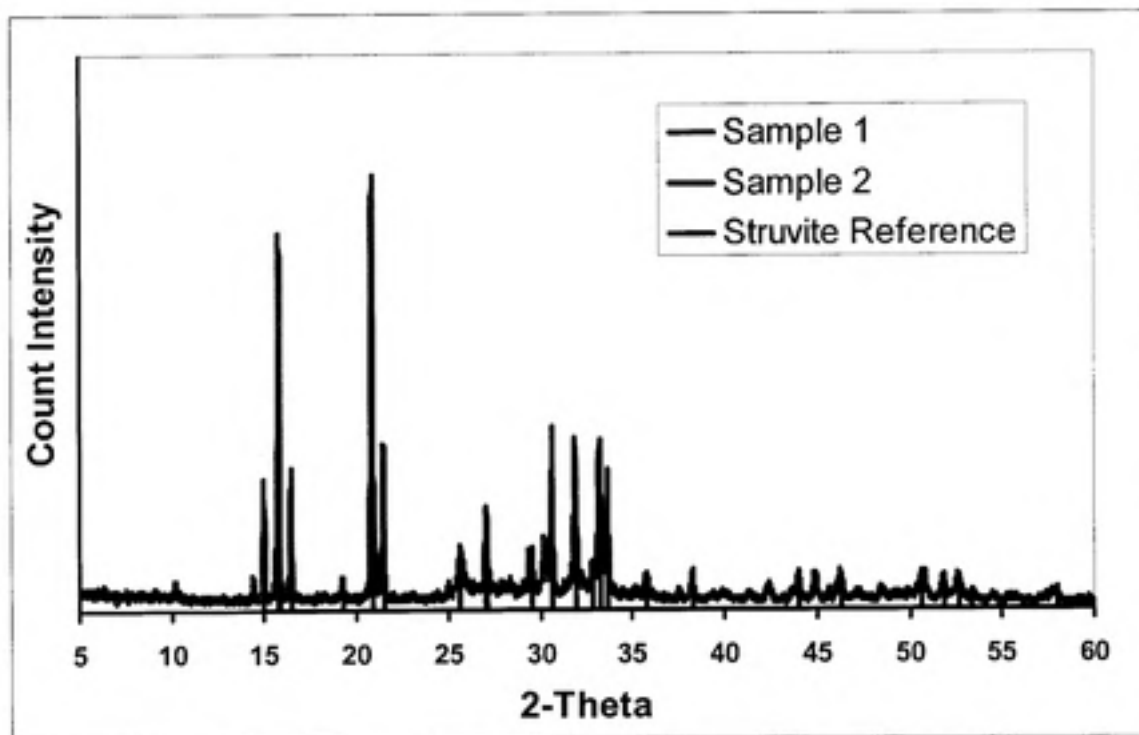


Figure 4.16 Comparison of XRD patterns of non-autoclaved non-oven-dried samples with struvite reference pattern.

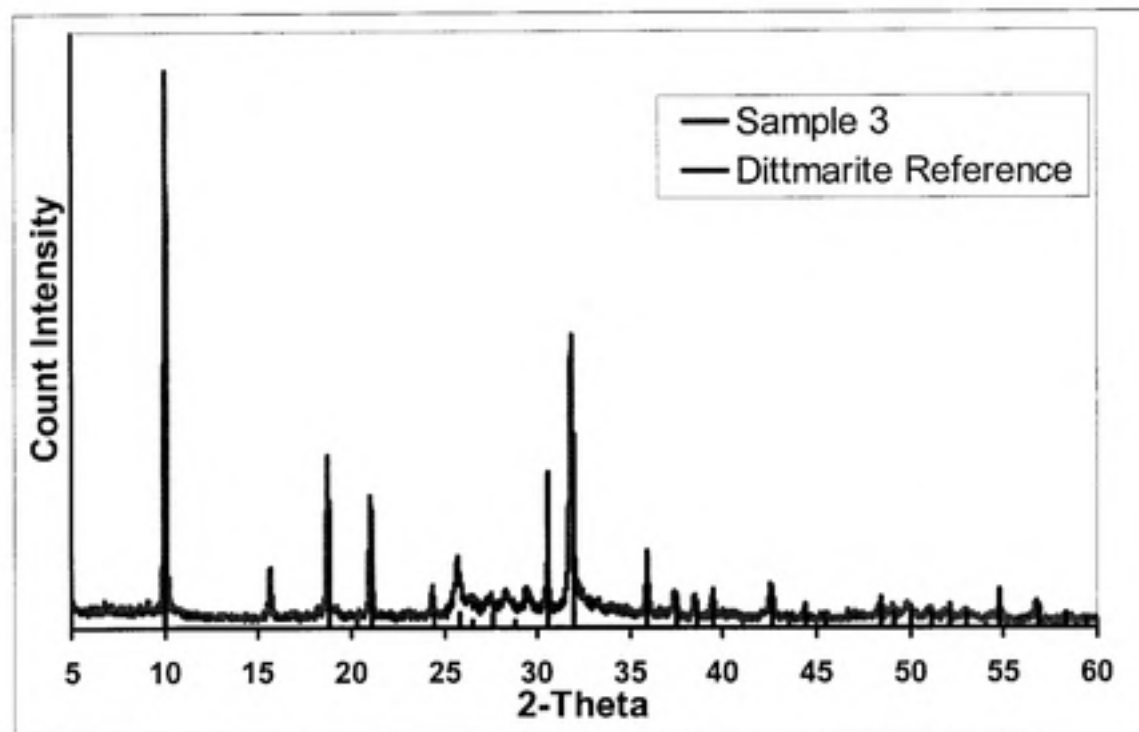


Figure 4.17 Comparison of autoclaved and oven-dried sample with dittmarite reference pattern

4.4 SEM analysis

To confirm the results of the XRD analysis, Scanning Electron Microscopy (SEM) was also performed. Figure 4.19 shows a photograph taken during the SEM analysis, in which two solid phases are clearly present. Plate-like structures appear to dominate. This may suggest the presence of struvite, which can appear in various crystal forms, including tabular and wedge-shaped. The second minor solid phase found in the photograph may be hydroxylapatite, which can have various habits including granular, globular, and nodular concretions (Roberts, 1990).

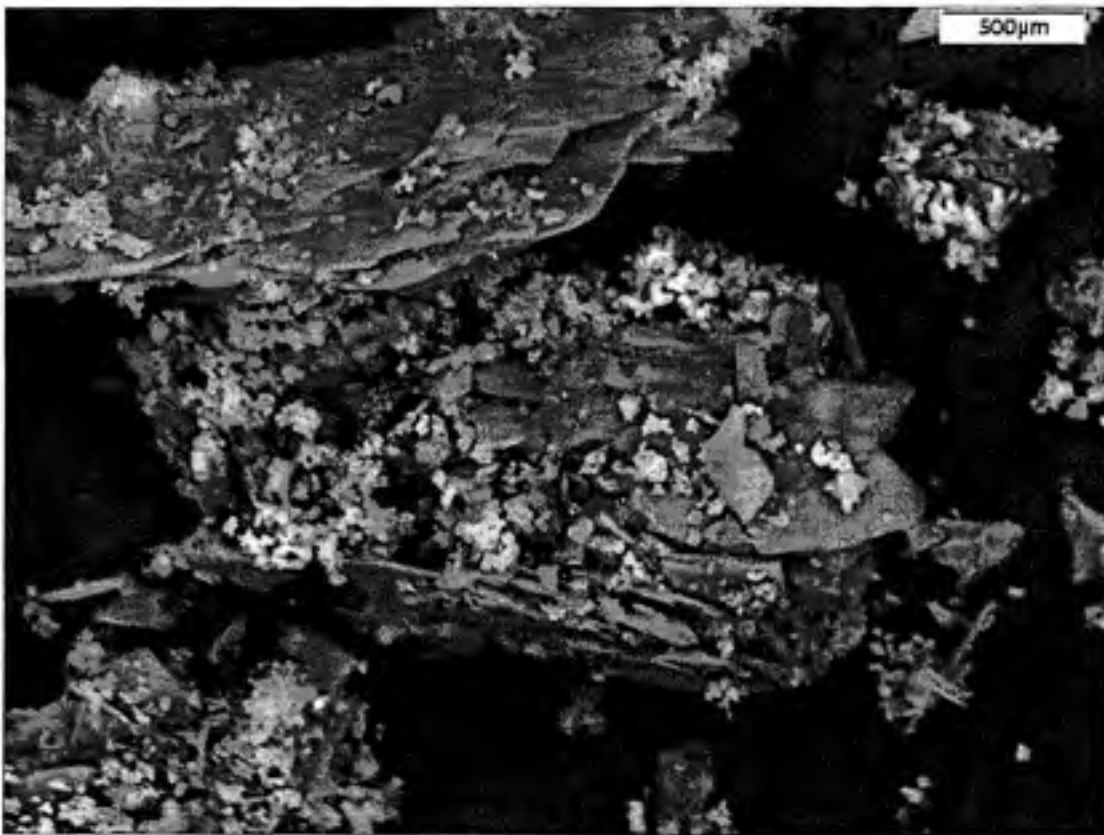


Figure 4.18 SEM photograph of deposit found in RDU Terminal A

The output from the SEM also provides an elemental analysis of the sample, giving the percentage composition by weight of some of the elements that are present in the sample. These elemental results are illustrated in Figures 4.20 and 4.21. Several regions on the same sample were measured in order to get a more accurate representation of the sample's composition. The inserts in each figure represents an average of four different measurements. For most samples that were analyzed, the SEM results showed significant percentages of magnesium, oxygen, phosphorus, and calcium. The average percentage of these four elements present in the sample was compared with the percentage of that element in pure magnesium ammonium phosphate (struvite). In both cases (see inserts in Figures 4.19 and 4.20), the percentages of Mg, O, and P are very similar to what they would be if the material were pure struvite. The presence of small amounts of calcium in the samples, as well as excess phosphorus, may indicate the presence of small amounts of calcium hydroxylapatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH})$) in the deposit as suggested by Figure 4.18. However, the XRD analysis did not show peaks that were consistent with this mineral.

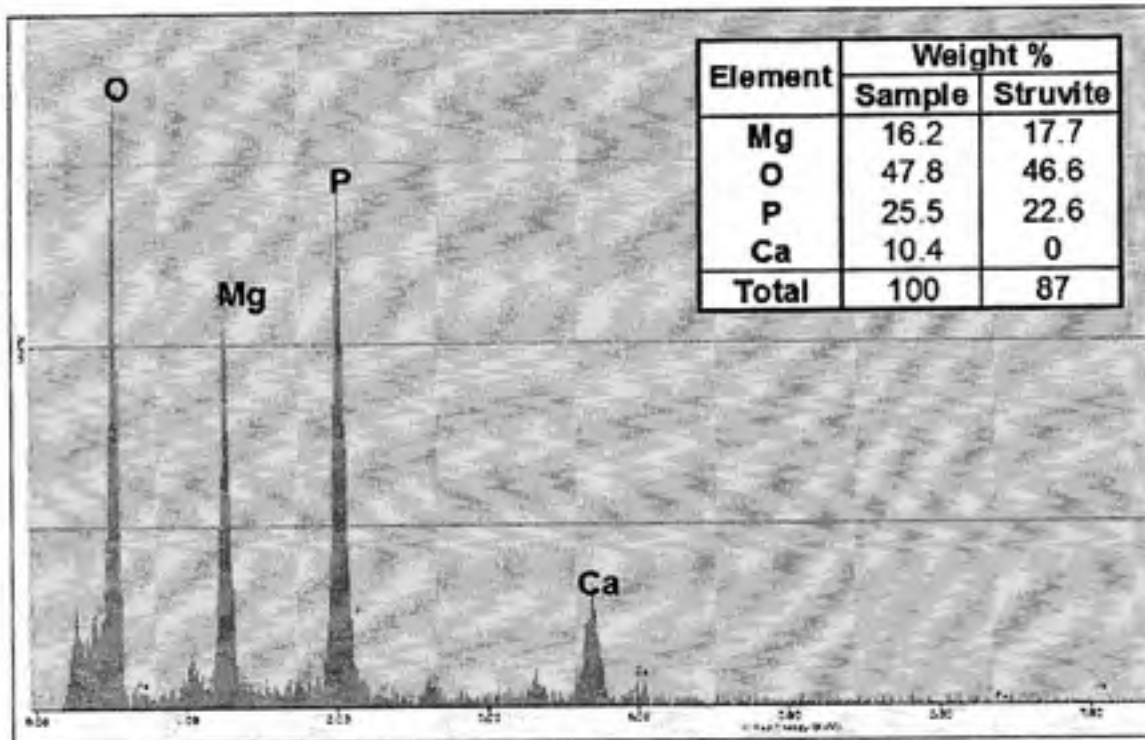


Figure 4.19 SEM results for RDU Terminal A sample, showing elemental composition to be similar to that of struvite

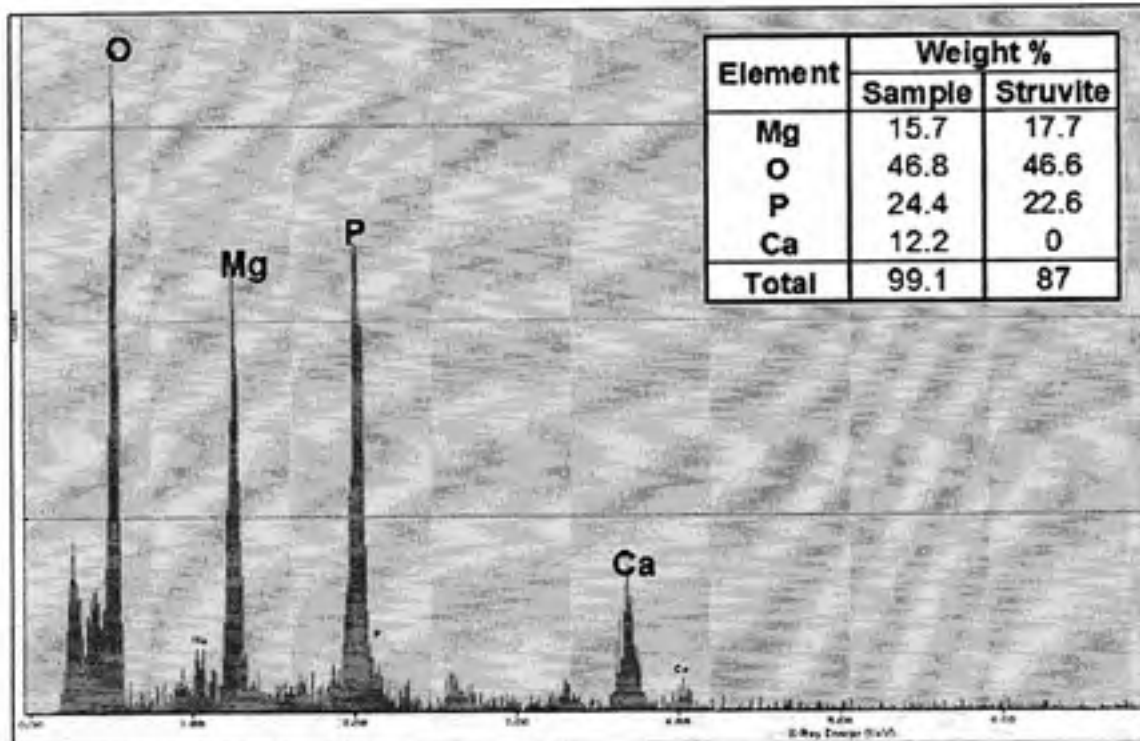


Figure 4.20 SEM results for FedEx Global Education Building 1st floor sample, showing elemental composition to be similar to that of struvite

Table 4.9 gives the results for each of the four measurements taken on each sample, along with the reference values for struvite. The average values match the composition of struvite reasonably well, as the standard deviations of the four measurements for each element are relatively small.

Table 4.9 Magnesium, Phosphorus, and Oxygen Content of Selected Samples

Percent Composition by Weight							
RDU Sample							
	STRUVITE	1	2	3	4	avg	stdev
Mg	17.7	13.6	16.3	18.8	16.0	16.2	2.1
P	22.6	23.6	24.8	26.3	27.2	25.5	1.6
O	46.6	46.1	47.4	48.8	48.9	47.8	1.3
Giles Horney Sample							
	STRUVITE	1	2	3	4	avg	stdev
Mg	17.7	14.0	0	22.5	9.3	15.3	6.7
P	22.6	29.4	20.4	24.0	20.7	23.6	4.2
O	46.6	49.9	41.4	47.9	44.0	45.8	3.8
Global Education Sample							
	STRUVITE	1.0	2	3	4	avg	stdev
Mg	17.7	9.0	21.4	16.7	2.1	15.7	6.2
P	22.6	23.8	24.4	25.1	4.4	24.4	0.7
O	46.6	44.9	48.0	47.6	66.8	46.8	1.7

4.5 Implications of Findings

The desire to limit water use, especially for growing communities with limited and, in some cases, dwindling water resources has caused many to look for new ways to conserve water. One way for institutional, commercial, and industrial establishments to decrease their demand for water is to install lavatory fixtures (faucets, toilets, and urinals) that have become increasingly efficient with respect to water consumption. This increasing efficiency of fixtures has been driven by more stringent federal regulations governing the maximum flows of faucets, toilets and urinals, as well as consumer awareness.

At UNC-Chapel Hill, 300 Waterfree urinals were installed in 2002 in an effort to conserve water during a drought and thereafter. In 2008, due to mineral deposition in the pipes behind the urinals and odor complaints, the decision was made to remove all Waterfree urinals on campus, replacing them with ultra-low flush devices. In order for non-water urinals to become a viable option for water conservation, the problem of mineral deposits in drain lines must be addressed.

One alternative to water-free urinals is the use of ultra-low flush urinals and high-efficiency urinals. Ultra-low flush urinals are those which meet the federal standard of 1.0 gpf, and high efficiency urinals use 0.5 gpf or less. Various models of high-efficiency urinals are available which use only one quart, one pint, or less than one pint of water per flush. While these new options are an improvement from the inefficient conventional flush urinals which use between one and five gallons per flush, from a water conservation perspective, a urinal which uses no water at all is clearly the most desirable option.

Given the wide array of non-water urinal types available, another option is to shift non-water urinal usage to types which do not lead to mineral deposits in the pipes. It has been shown in this study that certain types of cartridges are more likely to cause deposits than others. More deposit was found in urinal systems which had been using the Falcon Waterfree cartridges as opposed to the Eco cartridges. Although odor problems are still a concern for both types of cartridges, other urinal systems which do not use a liquid sealant should be considered. It is likely that a urinal system which allows for small amounts of water to be used for cleaning, or systems which could be flushed with water periodically, would limit the deposition of minerals in the drain line.

Another potential cause of pipe deposits is the slope of the drain line behind the urinal. In a conventional system, flushing water enters a drain pipe at a high enough flow rate to rinse out any standing urine. In a waterless device, urine tends to stay in the pipe between uses. This problem could be addressed in new construction and retrofits by installing drain pipes with steeper slopes, i.e. slopes greater than the 2% slope that is currently the minimum building code requirement. Such designs may be sufficient to prevent urine from standing in the pipes and causing mineral deposition. If necessary, the building code could be specifically modified to address water free urinals.

If the problems with mineral deposition can be overcome, there may be additional implications beyond those involving water conservation. The possibility of collecting and treating urine separately from the rest of the waste stream is an idea which has recently increased in popularity. It is seen as a possible way to improve efficiency and flexibility at wastewater treatment plants. About 75% of the nitrogen and 50% of the phosphorus at a municipal wastewater treatment plant comes from urine (Larsen & Gujer, 1996). Although urine is very high in nutrients, it makes up less than one percent of the total wastewater volume. This suggests that if urine were separated at the source, it could allow for nutrient recovery at wastewater treatment plants and could lead to reducing or eliminating the need for costly nutrient removal technologies such as nitrification, denitrification, and phosphorus removal (Maurer et al., 2006). A study performed by Wilsenach and van Loosdrecht (2006) showed that source-separated urine can be treated to high effluent quality standards while saving energy resources. In addition to improved wastewater treatment plant performance, there is potential to abate water pollution and recover valuable nutrient resources by implementing nutrient removal in source-separated

urine (Larsen et al., 2007). This source-separated urine can be treated using a variety of techniques, such as microfiltration, nanofiltration, reverse osmosis, nitrification, anammox (anaerobic ammonia oxidation), ammonia stripping, ion exchange, struvite precipitation, electrodialysis, and ozonation (Maurer et al., 2006). In addition to the challenges of effectively treating this separated urine, some obstacles to a successful urine source-separation system are the storage and transport of the urine, the building of new infrastructure, and well-designed waste-separating toilets and water-free urinals which do not lead to the types of mineral deposition problems described in this study.

Chapter 5

Conclusions and Recommendations

In an attempt to conserve water, many institutions, commercial establishments, and municipal facilities are increasing their use of water-saving devices, such as high-efficiency faucets, toilets and urinals. Consequently, the use of waterless urinals has become more widespread in the United States in recent years, but problems have been encountered, warranting a detailed inspection and analysis of their problems.

The conclusions of this study show that mineral deposits can occur in the drain lines behind waterless urinals. Deposits were documented in locations on the UNC-Chapel Hill campus and at RDU Airport, where waterless systems had been used for time periods as short as six months and as long as six years. It was also shown that deposits occurred in facilities that received very high usage, as well as those which received low usage.

Another conclusion of this study was that the extent of deposit was greater in facilities that had used Falcon Waterfree urinal cartridges than in facilities where only Eco cartridges were used.

Upon analysis of the mineral deposit samples collected, it was shown that the deposits which form in the drain lines of these urinals are composed primarily of struvite (magnesium ammonium phosphate). This determination was made using x-ray diffraction analysis and the results were confirmed using scanning electron microscopy.

Additionally, a chemical equilibrium model was used to simulate the hydrolysis of urea in the drain lines behind water-free urinals and determine the equilibrium pH of

the system as urea hydrolyzes. This model also showed that water-free urinal collection systems are oversaturated with respect to struvite, calcite, and calcium hydroxylapatite, indicating that these minerals are likely to deposit in these systems.

It has been shown that deposits occur in non-water urinal systems, and that some types of waterless devices cause more deposit than others. More research should be performed to determine the extent of deposition behind all commercially available urinals with different types of cartridges: liquid seal, mechanical seal, buoyancy bodies, and others which are marketed. It would also be beneficial to know the water savings of water-free urinals when compared to certain high efficiency urinals which may use one pint of water or less per flush. The potential of these high efficiency urinals to cause drain line deposits should also be determined. Additional research should investigate the effect of the slope of the drain line on the formation of mineral deposits.

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