URINE SOURCE SEPARATION: CRITICAL LITERATURE REVIEW AND NOVEL
PRECIPITATION CONTROL

By

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To Nancy and Lara

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LIST OF ABBREVIATIONS

ACP	Amorphous calcium phosphate
Ca/Ca^{2+}	Calcium
$CaCO_3$	Calcium carbonate
CER	Cation exchange resin
CSO	Combined sewer overflow
DI	Deionized
EDTA	Ethylenediaminetetraacetic acid
g	Gram or grams
HAP	Hydroxyapatite
HCO_3^-	Bicarbonate
I	Ionic strength
IAP	Ion activity product
IC	Ion chromatograph or ion chromatography
IX	Ion exchange
K	Potassium
KMP	Potassium ammonium phosphate
L	Liter or Liters
Mg/Mg^{2+}	Magnesium
mg	milligram
min	Minute or minutes
mL	Milliliter or milliliters
M	Molar
MAP	Magnesium ammonium phosphate

mM	Millimolar
N	Nitrogen
NH_3/NH_4^+	Ammonia/ammonium
OCP	Octacalcium phosphate
OH^-	Hydroxide
P	Phosphorus
PO_4/PO_4^{2-}	Phosphate
SI	Saturation index
SO_4^{2-}	Sulfate
μm	Micrometer
μL	Microliter
WWTP	Wastewater treatment plant

Abstract of Thesis Presented to the Graduate School
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Urine separation and treatment can provide many benefits, including nutrient recovery, reduced water and resource use, and lower capacity wastewater treatment plants. The environmental benefits are numerous but success of these systems depends greatly on process engineering and user acceptance. Laboratory scale studies have sought to optimize the recovery of a potentially valuable mineral, struvite, a magnesium phosphate mineral, from urine by precipitation. Few full-scale reactors for struvite precipitation have been implemented at this time. These units have shown good recovery of phosphorus but more research is needed to make them economically feasible and ensure maximum nutrient recovery.

Urine separating units are hindered by clogging due to mineral precipitation triggered by urea hydrolysis, a process catalyzed by the enzyme urease which transforms the urea into ammonia and bicarbonate. The two most common mineral precipitates are hydroxyapatite (HAP), a calcium phosphate mineral, and struvite. Problematic precipitation, along with other usability issues, has resulted in variable success of urine separation units.

Preliminary experiments were conducted to examine the removal of magnesium and calcium from synthetic urine using a cation exchange resin with the goal of preventing the formation of HAP and struvite. Cation exchange treatment showed good removal of both calcium and magnesium from the urine, with a preference for calcium. However, calculations showed that HAP and struvite were still supersaturated in the treated urine, which motivated subsequent precipitation studies. The goal of the precipitation studies was to study the rate and extent of mineral precipitation. A synthetic urine mixture was prepared to simulate urine after it had undergone cation exchange treatment and urea hydrolysis. Two batches of synthetic hydrolyzed urine were made: magnesium only and calcium only. The aged urine was dosed with different amounts of phosphate to observe the amount of calcium and magnesium precipitated from the urine. Results from the precipitation studies agreed with the stoichiometry for struvite precipitation (1:1 Mg:P) and HAP precipitation (5:3 Ca:P). This research is important because it provides new information about precipitation reactions in urine which is expected to improve the performance of waterless urinals and urine source separation technology.

CHAPTER 1
OVERVIEW OF THESIS

The overarching goal of this thesis was to systematically evaluate source separation and treatment of human urine by conducting a comprehensive review of the literature and conducting laboratory experiments. The literature review focused on environmental benefits, process engineering advances and challenges, and user attitudes and real-life efficiency. The laboratory experiments focused on mineral precipitation in urine, which remains a major obstacle to urine separation and treatment. Figure 1-1 shows the organization of thesis. Chapter 2 is the literature review. Chapters 3–6 present results from the laboratory research. Chapter 7 provides conclusions that span the literature review and laboratory research, and provides recommendations for future research.
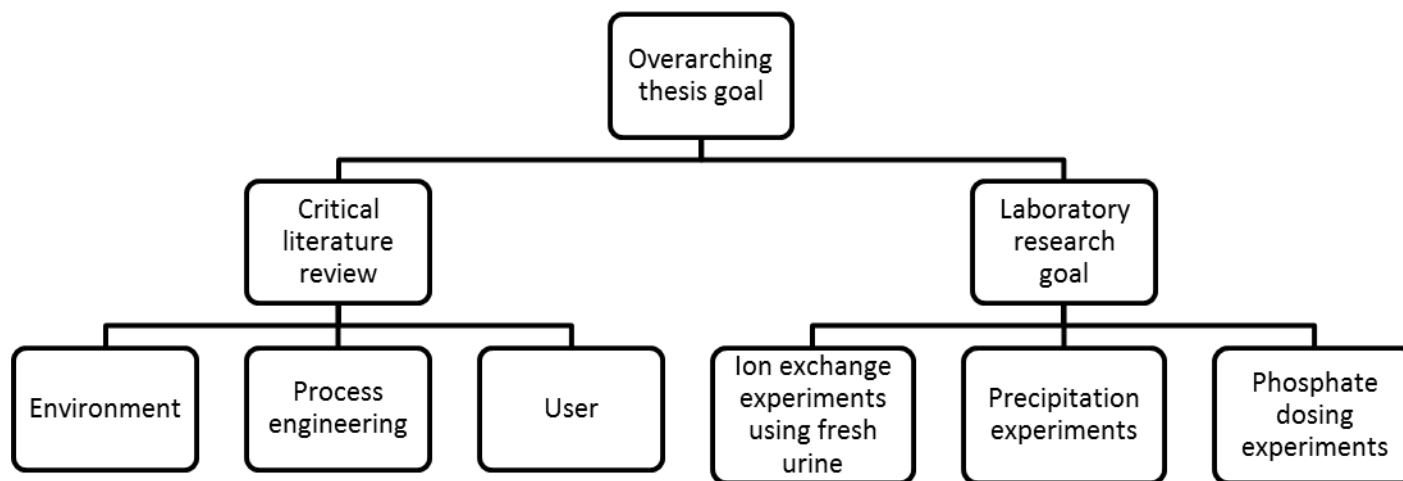
Figure 1-1.   Schematic showing organization of thesis.

CHAPTER 2
CRITICAL LITERATURE REVIEW

2.1 Overview and Objectives

Source separation and treatment of human urine has many advantages over the conventional approach to domestic wastewater treatment. At the highest level, urine separation and treatment can drastically reduce the load of nutrients to wastewater treatment plants, thereby saving energy and increasing the efficiency of treatment units. Nutrients that are currently discharged to the environment, from either incomplete treatment or leaks in the system, would be eliminated by separate collection and treatment of urine. Urine separation and treatment offers the possibility of recovering nutrients from urine for beneficial use, which is attracting increasing interest as mineral resources such as phosphate are becoming scarce and require increasing energy inputs for production. Unfortunately, there is not a clear consensus on the most effective collection and treatment scheme for urine separation and treatment. As a result, widespread implementation of urine separation and treatment is far from reality at current conditions. The environmental benefits of urine separation and treatment cannot be fully realized without reliance on innovative process engineering to overcome issues with implementation and user dependent success rates. Figure 2-1 illustrates the intersection of the environment, process engineering, and user in the context of conventional wastewater treatment and innovative urine separation and treatment.

This goal of the literature review was to provide new insight on a few aspects on the current states of urine separation and treatment. The environmental benefits and contributions to sustainable wastewater management are the key drivers for urine separation and treatment. However, many obstacles remain that hinder the realization

of urine separation such that innovative process engineering approaches are needed. Previous research on urine separation and treatment is vast with numerous attempts to optimize different processes for urine treatment. Struvite precipitation is the most widely studied process in urine treatment because of its potential to recover multiple nutrients from urine. As such, struvite precipitation was the focus of the process engineering section of the literature review. Finally, user dependent success was examined by reviewing the success of past urine separation projects and by looking at impediments to successful urine separation, specifically spontaneous precipitation.

2.2 Environment

The current approach to centralized municipal wastewater treatment consumes large amounts of freshwater, discharges nutrients to water bodies, does not properly remove potentially toxic endocrine disrupting chemicals and micropollutants (Larsen et al., 2001), and allows no option for resource recovery. The idea behind urine separation and treatment is that treating concentrated, unmixed solutions is more resource efficient then treating highly dilute combined solutions (Larsen and Gujer, 1997). Currently, NoMix toilets developed at the Swiss Federal Institute for Environmental Science and Technology provide an easy, effective way to separate urine and save about 80% of the water used in toilet flushing (Larsen et al., 2001). Waterless urinals can also be used to separate urine.

Urine contains over 80% of nitrogen, 50% of phosphorus, 90% of potassium in the total nutrient load to conventional wastewater treatment plants (Larsen et al., 2001). The removal of the nutrient load on wastewater treatment plants by separation and treatment of urine could provide many benefits. By removing urine before sending wastewater to the plant, influent carbon and nitrogen levels in the remaining wastewater

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would be ideal for removal of organic material and nitrogen by biological treatment

(Larsen et al., 2001). Separation of urine can also reduce the toxic effects of combined

sewer overflows that discharge into rivers and lakes (Larsen et al., 2001). Leaks from

the wastewater collection system introduce pollutants to the environment and threaten

groundwater quality (Larsen and Gujer, 2001), separation of urine, which contains 70–

80% of pharmaceuticals in these sewers, reduces this risk (Larsen and Gujer, 2001).

Nutrient treatment and release by traditional wastewater treatment plants also

eliminates the option of significant nutrient recovery and reuse. Limited phosphorus

resources and energy-intensive nitrogen fixation are important drivers for nutrient

recovery and reuse (Cordell et al., 2009; Larsen and Gujer, 2001; Hanaeus et al.,

1997). Recovery of the nutrients in source-separate urine could potentially eliminate the

environmental impacts associated with the production of synthetic fertilizers and

resource depletion (Larsen et al., 2001). Urine separating systems have been used in

Sweden for sustainable waste treatment and nutrient recycling since the 1990s

(Hanaeus et al., 1997). The original urine separation systems used a toilet, much like a

conventional toilet, but with a small unit for urine collection and a flush-water system for

this unit, the pipes lead to a storage tank that stored the urine for a period of eight

months maximum and then urine was directly applied to the local grazing fields

(Hanaeus et al., 1997). Since their inception these units have been modified to increase

usability and nutrient separation and collection. Real-world efficiency of both early

source-separating toilets and current models are discussed in section 2.4.

2.3 Process Engineering

The concept of urine source separation is very appealing for the reasons

described in the previous section. However, considerable development is needed to

fulfill the promises of urine source separation and treatment. Moreover, whether current technology will actually become a viable and economically attractive alternative to conventional wastewater treatment will depend greatly on technical improvements to applicable solutions (Larsen et al., 2010). Research is needed to determine both technical aspects of urine separation but also how it will be implemented into the existing infrastructure (Berndtsson, 2006).

Planning of the separation, collection, storage, and transportation aspects of urine source separation have been suggested. Early literature on source separation proposed storage of urine and conveyance to the wastewater treatment plant in waves, in order to create a smooth, even load of nutrients thereby reducing changes of harmful emissions to the environment (Larsen and Gujer, 1996; Larsen et al., 2009). However, current thinking is focused on decentralized, or onsite treatment as a more practical and economically feasible option. Technical progress and research can help develop these on-site technologies (Larsen et al., 2009). Many different options have been studied, but not many technologies have made it beyond laboratory scale testing. Different combinations of current process can achieve different goals but there has yet to be a consensus on what combination of these technologies will be the most beneficial and feasible.

2.3.1 Laboratory scale struvite precipitation research

Though direct application of urine to agriculture is the simplest, most obvious choice of nutrient reuse from urine, there are concerns about micropollutants and pathogens in urine that may have associated ecotoxicological risks (Larsen and Gujer, 2001). There is also concern that urine can increase the salinity of soils thereby decreasing soil fertility (Mnkeni et al., 2008; Karak and Bhattacharyya, 2011). In

addition, the concentration of nutrients in urine is lower than commercial fertilizers; as a result transportation of large volumes of untreated urine would be required at a considerable economic cost (Maurer et al., 2006; Pronk and Kone, 2009). As a result, treatment processes that can recover the nutrients in urine at a high concentration can eliminate many of the transportation issues as well as the risks associated with pathogens, micropollutants, and salinity. Successful treatment of source separated urine must also overcome the instability of urea, which upon hydrolysis, increase urine pH and results in ammonia loss and unpleasant odors (Larsen and Gujer, 1996). Hydrolysis of urea can also lead to precipitation that can hinder the usability of collection units and the success of subsequent treatment (see section 2.4 for a more information on urea hydrolysis). Options being considered for separate urine treatment include volume reduction using evaporation or freeze-thawing, removal of micropollutants by electrodialysis, and hygienization through storage, among many other processes (Maurer et al., 2006).

Recent research has suggested that precipitation and collection of struvite, a magnesium phosphate mineral ($NH_4MgPO_4 \cdot 6H_2O$), from source separated urine is an effective treatment technique (Larsen and Gujer, 1996; Lind et al., 2000; Maurer et al., 2006). Struvite could be used as a valuable source of fertilizer, and nearly close the cycle for phosphorus, which is known to become scare in the foreseeable future. Struvite precipitation is an attractive treatment for source separated urine as it contains two dominant nutrients, nitrogen and phosphorus, in solid form (Maurer et al., 2006) and it has shown potential to be used as a slow-release fertilizer (Bridger et al., 1962; El Diwani et al., 2007; Johnston and Richards, 2003). Additionally, the pH of completely

hydrolyzed urine, of pH 9 and above (Udert et al., 2003), is ideal for struvite precipitation (Buchanan et al., 1994).

Without the addition of magnesium, however, only about 27% of the phosphorus and 0.6% of the nitrogen found in urine will precipitate as struvite (Udert et al., 2003). This has led to a plethora of research into the optimum conditions, including magnesium addition, pH adjustment, phosphorus addition (for increased nitrogen removal), and dilution factors for struvite recovery from source-separated urine. Additionally, recent studies have examined the option of co-precipitation of potassium struvite. It can be concluded from Table 2-1 that at a magnesium to phosphorus ratio (Mg:P) of 1.5:1 in hydrolyzed urine, over 90% of phosphorus can be recovered as struvite regardless of pH. For unhydrolyzed, pH adjusted urine, the trend is less clear.

2.3.2 Implementation of struvite precipitation reactors

Though struvite precipitation technologies have been used to recover struvite from various waste streams, including anaerobic digester supernatant, chlorinated secondary effluents, swine wastewater, and liquors ((Le Corre et al., 2009) for a comprehensive review), few have been attempted with urine outside of the laboratory. Two reports of full-scale, struvite crystallization from source-separated urine have been tested as described below.

Antonini et al. (2008) studied the effectiveness of a struvite precipitation reactor, NuRec, using urine collected from one urine-separating toilet and 1 waterless urinal in a dormitory of 100 students. The NuRec system used magnesium oxide dosed at a magnesium to phosphorus ratio of 1.5:1; about 50 L of stored urine was treated at a time. Thirty minutes of mixing was followed by a 3 h sedimentation phase. The effluent was treated by stripping and absorption processes. The authors tested both diluted and

undiluted urine, containing phosphorus concentrations of 2.30 mg/L to 110.83 mg/L and 5.20 mg/L to 311.2 mg/L, respectively. For undiluted urine, about 100 g struvite could be recovered per batch, while only 32 g could be collected in diluted urine. Between 10–30 g of the struvite precipitate was lost during recovery as it remained trapped in the filter fibers. For diluted urine this translated to a loss of 91.5% of precipitation struvite, making the process unproductive.

Etter et al. (2011) studied the functionality of precipitating struvite from urine using a filtration reactor in a village in Nepal. The urine was collected using urine diverting dry toilets and had been stored and slightly diluted (due to cleaning of the toilets) before experimentation. Etter et al. (2011) used three different magnesium sources, magnesium sulfate, bittern (a waste stream from salt production), and magnesium rock. The reactor was made from sheet metal and consisted of a 50 L drum with a conical bottom, with a welded stirring mechanism that led to a filter bag through a ball valve. The filter chosen was nylon with a pore size of 160 μm. Struvite was precipitated from addition of magnesium in a magnesium to phosphorus molar ratio of 1.1:1 and 10 min of stirring; after which, the retained filter cake was dried. The reactor was able to removed 91% of the phosphate content of the urine. The time to process 50 L of urine took about 1 h and due to this low retention time struvite scaling on the reactor walls was not an issue. Etter et al. (2011) estimated that 1 kg of struvite could be recovered from 720 L urine at a 1:1 molar magnesium to phosphorus dosage.

The value of the effluent from the reactor, due to its high nitrogen and potassium concentration, has an estimated value of four times that of the struvite. Etter et al. (2011) suggests that direct application would be the easiest way through drip irrigation

systems, protecting from ammonia loss due to volatilization. However, direct application feasibility is limited and additional physical, chemical, or biological process could be necessary for effluent treatment. Both studies showed some success in recovery of struvite from undiluted urine, but improvements could be made to increase recovery. Effluent from the reactors required treatment, but could be used beneficially as fertilizer, as it contained high potassium and nitrogen levels.

2.4 User

The key for long term success of urine separation and treatment is user acceptance and attitudes toward the system. An increase in user motivation can be seen when users are supplied with knowledge regarding the benefits of urine separation (Berndtsson, 2006). User compliance and acceptance can also be increased with development and implementation of effective collection units. Collection units need to be easy to use, as user acceptance is a prerequisite for widespread use (Lienert and Larsen, 2010). This means overcoming many obstacles that currently detract users from urine separating units, including odors, maintenance issues due predominantly to clogging, and behavior modification.

2.4.1 Usability issues and problematic precipitation

Mineral precipitation in traps and pipes are the major cause of odor and blockages in urine collection systems (Hanaeus et al., 1997; Udert et al., 2003; Udert , 2003c; Larsen et al., 2009). The two minerals most commonly found in NoMix toilets and waterless urinals are struvite and hydroxyapatite (HAP) (Udert et al., 2003). HAP is a calcium phosphate mineral, $Ca_5(PO_4)_3(OH)$. The enzyme urease, which are abundant in urine collecting systems, induces a process known as urea hydrolysis (or ureolysis) in

which the urea in urine is decomposed into bicarbonate and ammonium and triggers an

increase in pH (Udert et al., 2003). The urea hydrolysis reaction can be written as:

$$NH_2(CO)NH_2 + 2H_2O \rightarrow NH_3 + NH_4^+ + HCO_3^- \tag{2-1}$$
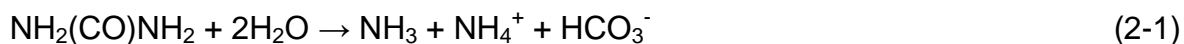
The increase in pH and ammonium concentration results in the formation of struvite and

HAP. Complete urea hydrolysis can be achieved in a little more than 1 day in urine

collecting systems containing urease (Udert, 2003c), but only about 2.5% and 20% of

ureolysis is necessary to reach the saturation limit for struvite and HAP, respectively

(Udert, 2003b; Udert et al., 2003). In a few hours of storage, undiluted urine can

spontaneously precipitate nearly all of its calcium and magnesium and about 27% of the

phosphate (Udert, 2003c). Not all of the precipitation takes place in the collection

system but also occurs in the pipes and traps of the system, which causes blockages

and odor problems. Importantly, the precipitation of these nutrients before reaching the

urine collecting system also reduces their availability for later recovery and use as

fertilizer (Udert et al., 2003).

Several options have been suggested to reduce the precipitation of HAP and

struvite in the plumbing of urine-separating toilets and waterless urinals. Periodic

cleaning with caustic soda or a mechanical snake (Jonsson, 2002) to clear blockages is

effective, but may not be suitable for high-use or public units. Preventing urea

decomposition with sulfuric acid (Hellstrom et al., 1999) and urease inhibitors in urine

storage has been examined. Self-cleaning surfaces to prevent biofilm build-up and

subsequent biological activity is another option for precipitation prevention (Barthlott and

Neinhuis, 1997; Moriyama et al., 1998; Li et al., 2007). Alternatively, forced precipitation

in removable traps which can be exchange and cleaned periodically can be another way

of preventing blockages (Udert et al., 2003), however it may be a challenge to develop a device small enough to be integrated into the toilet and allow for good interface between user and technology (Larsen et al., 2009).

Removal of magnesium and calcium from urine prior to entering the urine plumbing system has the potential to reduce odors and blockage and assist with the controlled production of struvite. Without magnesium and calcium, less phosphorus will be bound in spontaneous precipitation and allow for more struvite formation per volume of urine, increasing the desired product and nitrogen removal. Furthermore, removing calcium preferentially to magnesium will increase the magnesium to calcium ratio above 0.9, which is necessary for guaranteed struvite formation (Abbona et al., 1986). Tilley et al. (2008) showed that precipitation work done on post-spontaneous precipitation urine (i.e., only 15% of the original calcium and magnesium found in urine) was ideal for magnesium dosing and production of 99.5% calcium-free struvite. Etter et al. (2011) estimated that 40% more struvite could be collected in a urine treatment unit if spontaneous precipitation was prevented.

2.4.2 Overview of real-life systems

The most widely used source separation technologies are NoMix toilets and waterless urinals. These units are designed to provide low dilution of the urine and show comparable functionality to standard flush toilets and urinals. Ideally, these units would be able to collect 80% of the nitrogen and 50% of the phosphorus load of wastewater treatment plants, however nutrient collection in real life systems is far from ideal. Many researchers have studied these factors in urine separation and nutrient collection efficiency. Hanaeus et al. (1997) monitored the efficiency of nutrient collection in a urine separation system in a village in Sweden. The 55 person village collected the urine into

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three storage tanks for later reuse as fertilizer by direct application. The nutrients

collected during the study period can be seen in Table 2-2; the authors estimated that

the system collected between 2.8–3.7 g total nitrogen and 0.16–0.18 g total phosphorus

per person per day, which assuming that 70% of toilet visits occur at home, indicates

urine separation efficiency between 50–60%. In the storage tanks urine has a high pH

and 85–90% of the nitrogen appeared as ammonia, which indicates the potential loss of

nitrogen through ammonia volatilization. Loss of nutrients was also attributed to the

contamination of the urine collecting unit with flush water from the solid waste portion,

along with leakages of water into the urine collecting system.

   Rossi et al. (2009) studied the efficiency of urine separation in four apartments

equipped with NoMix toilets for one year. The NoMix units had a separate urine

collecting unit, which upon flushing, closed to prevent dilution. The toilets had two flush

levels of 3 and 6 L of water for the back portion of the toilet. They also reported the

values for a men's and women's restroom at an office, consisting of a NoMix toilet

whose urine outlet received 8 mL of flush water, and a waterless urinal. The authors

measured the collection of about 138 mL of urine/flush in the apartments, and 225

mL/usage and 309 mL/usage in the men's and women's restrooms, respectively. The

reported nutrients collected can be seen in Table 2-2. The authors reported a low

amount of urine collection per use when compared to expected urine volume; they

attributed this to flaws in the measurement of toilet uses as they can be used for other

purposes (i.e., waste disposal) and misuse of the two flush choices. The men's

restroom had better urine collection due to the fact that 76% of the men visited the

waterless urinal, in which close to no urine is lost. A low nitrogen to phosphorus ratio

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suggests nitrogen losses in the urine conducting pipes. The authors estimate that urine recovery in household to be between 70–75% of expected quantity, leaving room for technical and behavior improvements.

Vinnerås and Jönsson (2002) studied the efficiency of a system that included both urine and feces diversion. The study used Dubbletten urine diverting toilets. The system uses two, well-separated bowls and two flushing systems that are independent of one another. The large bowl, for feces, has a bulge which prevents an overflow of the flushing water into the front urine bowl. The authors studied 35 people for a period of 35 days. It was determined that 68% of the urine was collected, with the remaining fraction falling into the rear bowl. The collected and measured nutrients values were extrapolated to give an estimation of possible nutrient recovery from one person per year, which can be seen in Table 2-2.

In another study by Jonsson et al. (1997), using early urine-separating toilets, the authors found no evidence of ammonia loss through ventilation and a nitrogen to phosphorus molar ratio of 11.6:1. In the storage tank 86, 81 and 104% of the expected amount of nitrogen, phosphorus and potassium, respectively, were collected. The discrepancies in nitrogen and phosphorus are explained by a small amount of urine falling into the rear bowl and a high percentage of vegetarians. In this study, only 0.34 L of water per inhabitant and day were used, keeping the solution dilute and cut water consumption in half, compared to conventional toilets.

If the urine separating units are hard to use and require a large effort by the user, nutrient separation drops (Jonsson, 2002). Many users were detracted from the need to sit while urinating (Jonsson, 2002; Rossi et al., 2009), which is a necessity on many

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NoMix units. Each of the studies reported various technical problems with the urine collecting units or piping but one consistent conclusion was that success was dependent upon user motivation and dedication.

Environment	Process Engineering	User
•Impact of nutrient discharge •Sustainable nutrient production •Energy savings •Water use reduction	•Process optimization •Feasibilty/costs •Current applications •Change in nutrient quality •Handling/transportation issues	•Separation efficiency •User attitude/acceptance •Maintanance/usability issues
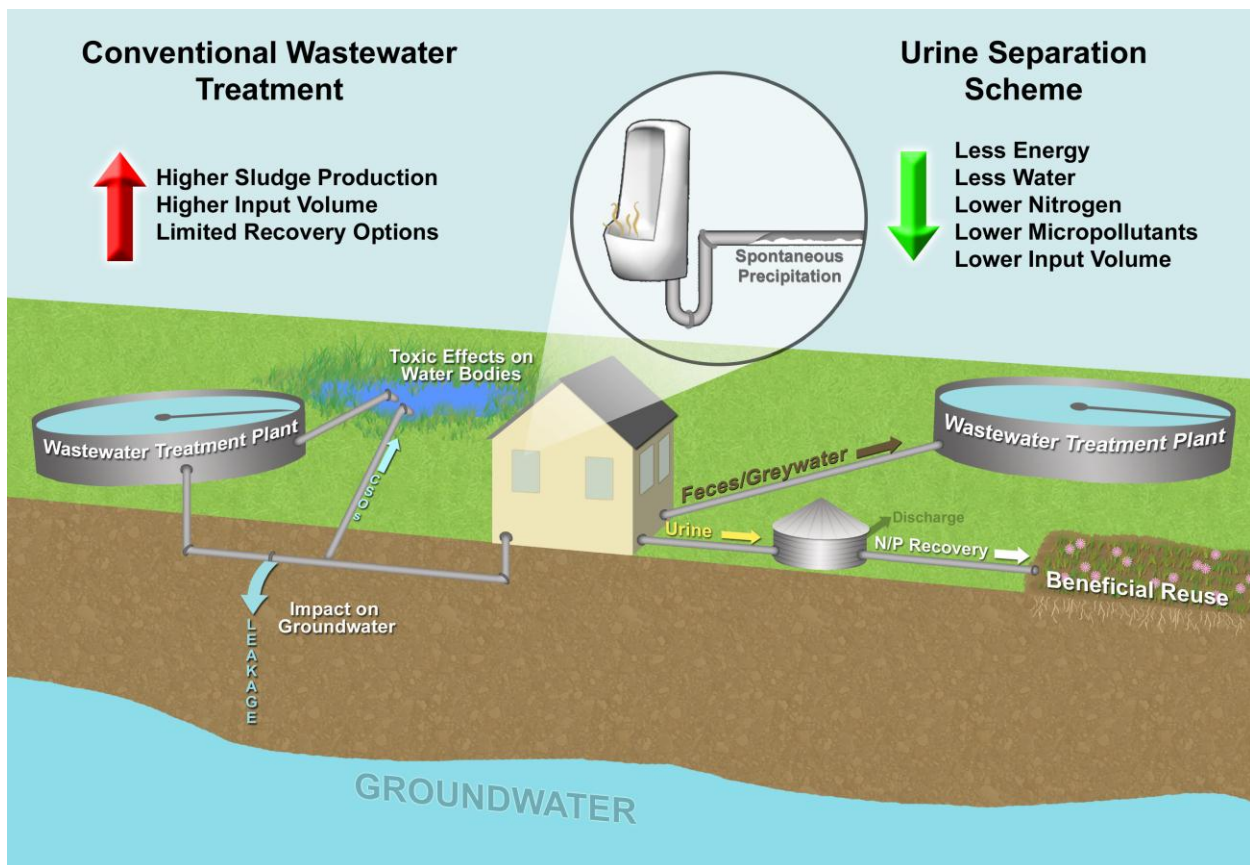
Figure 2-1. Different urine separation topics as related to the environment, process engineering and the user. Schematic to show factors affecting these three aspects in both conventional wastewater treatment and the proposed urine separation scheme.

Table 2-1. Overview of laboratory struvite precipitation experiments in the literature.

	Source	Aged?	Precipitation method	pH adjustment	P removal/recovery	P removed as	N/K removal/recovery	Mixing Conditions	Other/notes
(Wilsenach et al., 2007a)	Synthetic urine + additional P	Yes, with urease addition	Addition of MgO / MgCl$_2$ for Mg:P = 1 Mg:P = 0.75	Constant pH of 9.4 due to urease	99% P removal ≈73% P removal	MAP		Stirred and unstirred	
	Synthetic urine- no urea and low NH$_4$Cl (40mg/L N)	No, represented post nitrification-denitrification of urine	Addition of MgCl$_2$ for Mg:P =0.5:1 Mg:P = 1:1 Mg:P = 1.5:1 Addition of MgO for Mg:P =0.5:1 Mg:P= 1:1	None	≈55% P removal ≈74% P removal ≈75% P removal ≈50% P removal 100 % P removal	KMP			
(Liu et al., 2008)	Real human urine	Yes, mixed for 15 days	Addition of MgCL$_2$ for Mg:P 1.0:1 1.3:1 1.5:1	none	85% P recovered 95.7% P recovered 97.9% P recovered	MAP	3.7% N recovered 5.9% N recovered 5.3% N recovered	G= 150, 2 hours mixing	N/P constant at 84.3:1
			Addition of MgCL$_2$ and Na$_2$HPO$_4$ for Mg:N:P of 1.2:1:1 1.3:1:11	pH of 8.5 with NaOH	85.1% P recovered 94.1% P recovered	MAP MAP	95.7% N recovered 95.1% N recovered		
(Kabdasli et al., 2006b)	Real human urine	No	MgCl$_2$ and NaH$_2$PO$_4$ to dose to Mg:N:P 1:1:1	Yes, NaOH and H$_2$SO$_4$ to pH= 7.5 pH= 8 pH = 8.5 pH= 9 pH = 9.5	89% P removal 90.75% removal 97.66% removal 98.9% removal 99.3% removal	MAP	22.5% removal NH$_3$ 41.2% removal NH$_3$% 46% removal NH$_3$ 48 removal NH$_3$ 51.9% removal NH$_3$	Yes, slow mixing for 48 hours	

Table 2-1. Continued

	Source	Aged?	Precipitation method	pH adjustment	P removal/recovery	P removed as	N/K removal/recovery	Mixing Conditions	Other/notes
(Ronteltap et al., 2007)	Real human urine	Yes, naturally in urine collecting unit	$MgCl_2$ for apx PO_4-P:Mg of 1:1.5	No	100% removal of PO4-P	MAP		Yes, stirred for 3 hours	>98% hormones and pharmaceuticals in solution, and 20-63% of added heavy metals precipitated with struvite
(Ronteltap et al., 2010)	Real human urine	Yes, in storage tank	$MgCl_2$ for ratio of P:Mg of 1:1.5	Yes, with NaOH /HCl For pH=7 pH=7.5 pH= 8 pH= 8.5 pH=9 pH=10 pH=11	92.2% removal 94.1% removal 97.3% removal 98.4% removal 99.4% removal 99.4% removal 99.5% removal	MAP		Yes, 75 mins	Average crystal size= 74 μm 126 μm 136 μm 121 μm 92 μm 90 μm 129 μm
(Kemacheevakul et al., 2011)	Real human urine	No	pH induced; initial of urine Mg/P <1	NaOH/ H_2SO_4 pH= 9 pH= 10 pH= 11	26.19% recovery 29.04% recovery 31.06% recovery	MAP		200 rpm, 1 min, and 20 rpm for 20 mins	
(Tilley et al., 2008)	Synthetic urine	Yes , with urease	Dosed with PO_4: Mg ratio of 1:1 or 1:2	pH above 8	Between 80-93% P in struvite, no real trend with ratios			Shaken for 1 minute, reacting for 1 hour	Spontanteous precip filtered out, dilutions also examined
(Lind et al., 2000)	Synthetic urine	No	Dosed with MgO for Mg:P of 1:9.72 1:3.24 1:1.62	None	100% P removal 100% P removal 100% P removal	Struvite, written as [(Ca,Mg)(K,NH4) (PO4)·6H2O]	22% K removal 35% K removal 64% K removal		2% Ca removal 3% Ca removal 5.6% Ca removal

Table 2-1. Continued

	Source	Aged?	Precipitation method	pH adjustment	P removal/recovery	P removed as	N/K removal/recovery	Mixing Conditions	Other/notes
(Xu et al., 2011)	Synthetic urine	Yes; removal of ammonium /carbonate	Dosed with Na_2HPO_4, and $MgCl_2$ for Mg:K:P ratio of 1.6:1:1.6	NaOH for pH adjustment to : pH = 7 pH = 8 pH = 9 pH = 10 pH = 11 pH = 12	≈78% P removal ≈94% P removal ≈96% P removal ≈98% P removal ≈98.8% removal ≈99% P removal	MPP	≈27% K removal ≈58% K removal ≈62% K removal ≈66% K removal ≈66.6% removal ≈57% K removal	200 rpm for 20 minutes mixing time and 20 minutes sedimentation time	
			1.6:1:2 2:1:2 2.5:1:2 2:1:1.6 2:1:2.5	Yes, pH adjusted to 10 with NaOH	≈81% P removal ≈98% P removal 100% P removal ≈100% P removal ≈79% P removal		≈69% K removal ≈76% K removal ≈64% K removal ≈55% K removal ≈80% K removal		
		Yes; removal of carbonate plus 40 mg/L NH_4-N	Dosed with Na_2HPO_4, and $MgCl_2$ for Mg:K:P ratio of 2:1:2	Yes, pH adjusted to 10 with NaOH	≈98% P removal		≈76% K and ≈96% NH_4 removal		
		100 mg/L NH_4-N			≈98.2% P removal		≈74% K and ≈95% NH_4 removal		
		300 mg/L NH_4-N			≈98.4% P removal		≈66% K and ≈81% NH_4 removal		
		500 mg/L NH_4-N			≈98.6% P removal		≈65% K and ≈74% NH_4 removal		
(Darn et al., 2006)	Human Urine	No	pH adjustment		27% of P in solids at pH 8-10	MAP		none	
(Basakcilardan-Kabakci et al., 2007)	Human Urine	No	Mg: P = 1:1	pH = 9	94.3% P removal	MAP plus calcium precipitates	35% NH_3-N removal	1600 min^{-1} for 30 minutes	
				pH = 9	95% P removal		37.5% NH_3-N removal	1600 min^{-1} for 60 minutes	
				pH = 9	96% P removal		40% NH_3-N removal	1600 min^{-1} for 120 minutes	
				pH= 10	96.2% P removal		38% NH_3-N removal	1600 min^{-1} for 30 minutes	
				pH = 10	97.3% P removal		40.2% NH_3-N removal	1600 min^{-1} for 60 minutes	
				pH = 10	97.5% P removal		42% NH_3-N removal	1600 min^{-1} for 120 minutes	

Table 2-1. Continued

	Source	Aged?	Precipitation method	pH adjustment	P removal/recovery	P removed as	N/K removal/recovery	Mixing Conditions	Other/notes
(Basakcilardan-Kabakci et al., 2007)	Human Urine	No	Mg:P = 0.4:1	pH = 9	68.7% PO_4-P removal		≈ 34 % NH_3-N removal	1600 min^{-1} for 60 minutes	≈ 73.5 % Ca removal
				pH = 9.5	≈ 92 % PO_4-P removal		$\approx 49\%$ NH_3-N removal		≈ 99 % Ca removal
				pH = 10	≈ 96 % PO_4-P removal		≈ 47 % NH_3-N removal		≈ 99 % Ca removal
				pH = 10.7	97% PO_4-P removal		≈ 47 % NH_3-N removal		≈ 99 % Ca removal
	Human Urine	No	Mg:P = 1.3:1	pH = 9	≈ 93.5 % PO_4-P removal		≈ 44 % NH_3-N removal		60.7 % Ca removal
				pH = 9.5	≈ 94 % PO_4-P removal		≈ 40 % NH_3-N removal		≈ 99 % Ca removal
				pH = 10	≈ 98 % PO_4-P removal		≈ 30 % NH_3-N removal		≈ 99 % Ca removal
				pH = 10.7	≈ 99 % PO_4-P removal		≈ 30 % NH_3-N removal		71.9 % Ca removal
	Human Urine	No	Mg:P = 0.4:1	pH = 9	≈ 66 % PO_4-P removal		≈ 35 % NH_3-N removal		≈ 75 % Ca removal
			Mg:P = 0.6:1		≈ 93 % PO_4-P removal		≈ 42 % NH_3-N removal		≈ 93 % Ca removal
			Mg:P = 0.65:1		≈ 97 % PO_4-P removal		≈ 37 % NH_3-N removal		≈ 93 % Ca removal
			Mg:P = 0.85:1		≈ 98 % PO_4-P removal		≈ 37 % NH_3-N removal		≈ 86 % Ca removal
			Mg:P = 1:1		≈ 96 % PO_4-P removal		≈ 37 % NH_3-N removal		≈ 64 % Ca removal
			Mg:P = 1.2:1		≈ 96 % PO_4-P removal		≈ 38.5 % NH_3-N removal		≈ 66 % Ca removal
			Mg:P = 1.3:1		≈ 96 % PO_4-P removal		≈ 44 % NH_3-N removal		≈ 60 % Ca removal
			Mg:P = 1.57:1		96% PO_4-P removal		52.5% NH_3-N removal		66 % Ca removal

Table 2-1. Continued

	Source	Aged?	Precipitation method	pH adjustment	P removal/recovery	P removed as	N/K removal/recovery	Mixing Conditions	Other/notes
(Basakcilardan-Kabakci et al., 2007)	Human Urine	No	Mg:P = 1.8:1		$\approx$ 98 % PO_4-P removal		$\approx$ 49% NH_3-N removal		$\approx$68 % Ca removal
			Dosed with Na_2HPO_4, and $MgCl_2$ for Mg:P:N of 1.1:1.1:1	Adjusted with NaOH for pH=8	87.8% P removal	Mostly pure MAP. Approximately 0.12% and 0.33% Ca and K in solids	94.7% N removal	120 r/min	
			1.3:1:1	pH= 9.5	99.8% P removal		91.3% N removal	60 r/min	
			1.3:1.1:1	pH= 8.5	99.8% P removal		98.4% N removal	120 r/min	
			1.1:1:1	pH= 10	99.8% P removal		93.9% N removal	60 r/min	
			1.2:1:1	pH= 8	99.9% P removal		92.4% N removal	120 r/min	
			1:1.1:1	pH= 9.5	77.6% P removal		91.4% N removal	60 r/min	
			1:1:1	pH= 8.5	79.5% P removal		88.7% N removal	120 r/min	
			1.2:1.1:1	pH= 10	99.8% P removal		96.9% N removal	60 r/min	
			1:1.15:1	pH= 8	70.7% P removal		89.0% N removal	60 r/min	
			1.2:1.05:1	pH= 9.5	99.9% P removal		96.6% N removal	120 r/min	
			1.2:1.15:1	pH= 8.5	98.2% P removal		99.0% N removal	60 r/min	
			1:1.05:1	pH=10	79.4% P removal		90.2% N removal	120 r/min	
			1.3:1.05:1	pH= 8	99.8% P removal		93.2% N removal	60 r/min	
			1.1:1.15:1	pH= 9.5	79.7% P removal		96.2% N removal	120 r/min	
			1.1:1.05:1	pH= 8.5	92.6% P removal		95.5% N removal	60 r/min	
			1.3:1.15:1	pH= 10	99.9% P removal		98.8% N removal	120 r/min	

Table 2-2. Overview of results in the literature of real life urine separating systems and efficiencies.

	Population	System/Piping	Tank	Nutrients Collected/Percent of expected	Separation /Recovery Efficiency	Issues	Reuse
(Hanaeus et al., 1997)	55- 60% adults	Urine separating toilets, PVC pipes, 1800m of pipe to storage tank	3 tanks, 10m3, 5m3, and 10m3	Tot-N g/L – tank a/b/c= 0.54,2..84,1.38; NH4-N g/l 0.46,2.51,1.17 Tot-P: 0.031,0.169, 0.066	50-60% separation and 50% collected and transported	High dilution from flush water seep into urine section; leakage into urine sewer system	Direct app to field
(Rossi et al., 2009)	10 people, 4 apartments, 1 child and	NoMix plus waterless urinals	200-L storage tank	Household: NH_4 gm^{-3}: 1905 Ngm^{-3}: 2259 PO_4 gm^{-3A}: 387 $TotP$ gm^{-3}: 430 Men's NH_4 gm^{-3}: 5027 PO_4 gm^{-3}: 232 Women;s: NH_4 gm^{-3}: 3795 Ngm^{-3}: 4590 PO_4 gm^{-3}: 200	53% of average bladder voiding volume collected in households; 86% in men's bathroom;	Nitrogen losses in urine piping system	
(Jonsson, 2002)	315 people	BB Dubbletten and Worst Man Ecology DS		%Urine N collected: BB Dn 61% WM Ds: 65% %Urine P: BB Dn: 59% WM Ds: >65% % Urine K: BB Dn : 75% WM DS:58		Problems with precipitation in u-bend	Direct application to field
(Berndtsson, 2006)	125 inhabitants	Worstman Ecology DS	Two tanks with volumes of $60m^3$ and $15m^3$	N-tot: 313.5 kg/year; 50% of theoretical P-tot: 28.5 kg/year; 40% of theoretical		User complaints of smell	Direct reuse
(Jonsson et al., 1997)	44 apartments, 160 persons	Separating toilet; front bowl with small spray nozzle	Two tanks, 40 m3	N tot mg/l: 3631 Nh3/Nh4-N mg/l: 3576 P tot mg/l: 313 K tot: mg/L: 1000	86% N 81% p 104% K		
(Vinnerås and Jönsson, 2002)	18 apartments, 34 adults, 1 child	Dubbletten urine diverting toilets		N : 3741 g/person-year P: 340 g/p-y K: 1186 g/p-y			

^{A}: PO_4 does not include precipitated amount

CHAPTER 3
LABORATORY RESEARCH GOALS, OBJECTIVES AND LIMITATIONS

The overall goal of this research was to determine whether cation exchange can effectively remove calcium and magnesium from urine and subsequently lower the amount of pipe-clogging precipitates formed upon urea hydrolysis. The research was accomplished by completing the following tasks. First, jar tests were used to quantify magnesium and calcium removal from fresh synthetic urine at a range of cation exchange resin (CER) doses. Second, experiments with hydrolyzed synthetic urine were used to determine whether the calcium and magnesium removal achieved by CER changed the composition and mass of precipitates from that found in previous studies of urine precipitation. This included measuring the concentration of species before and after urine precipitation and tracking the change in precipitation mass. Third, experiments evaluated precipitation in hydrolyzed urine along a range of phosphate dosages. For all experimentally determined data, laboratory results were compared with modeling results in order to determine the effectiveness of chemical modeling programs for use in urine.

Experiments with urine often are subject to many limitations that may hinder the effectiveness, reproducibility, and implementation of the results. First, urine is a very concentrated solution with high ionic strength that presents difficulties when using analytical instruments and methods generally used on natural waters. Preparation of synthetic urine is also difficult due to spontaneous precipitation and complexation reactions. For instance, the fresh synthetic urine used in this project could not contain phosphate because of uncontrolled precipitation. Furthermore, the hydrolyzed synthetic

urine containing calcium could not include bicarbonate due to formation of calcium

carbonate. Fundamentally, the goal of producing a general synthetic urine recipe is

flawed because of the high variance in urine values found throughout the literature.

Urine also contains various organic complexing agents which are difficult to identify and

quantify in the literature (Brown et al., 1994). The presence of these complexing agents

may play a role in precipitation that is unable to be reproduced in the lab. Real-life

implementation of urine precipitation studies are further limited by the chemical

alteration caused in the non-sterile environments of urine collecting systems (Maurer et

al., 2006).

CHAPTER 4
MATERIALS AND METHODS

The objectives of the project were carried out in three different experiments referred to as Ion Exchange Experiments using Fresh Urine, Precipitation Experiments in Simulated Hydrolyzed Urine, and Phosphate Dosing Precipitation Experiments. Below, Figure 4-1, shows a brief overview of the experiments.

4.1 Ion Exchange Experiments using Fresh Urine

4.1.1 Fresh synthetic urine

A synthetic urine was made to contain the constituents found in fresh human urine as described in (Udert, 2003b). A commercial synthetic urine (Ricca Chemical Company) was used as the base solution for the fresh synthetic urine (hereafter Ricca urine). The Ricca urine was a very simple mixture and lacked many of the constituents found in fresh human urine and those it did contain varied in concentration level. A number of synthetic urine formulations were made and analyzed in the laboratory. The goal was to make the synthetic urine as similar in chemical composition to fresh urine as possible with particular focus on matching the magnesium and calcium concentrations. Many of the formulations caused immediate precipitation in the solution. Unwanted precipitation was avoided by not adding phosphate to the synthetic fresh urine. The final synthetic fresh urine was prepared by adding NH_4Cl, $(NH_4)_2SO_4$, and urea to Ricca urine. A comparison between the constituents and concentrations found in fresh human urine and those contained in the final synthetic fresh urine can be seen in Table 4-1. The ion concentrations in the urine mixture were checked by both ion

chromatography and titrations, as described in detail below. The synthetic urine was filtered and stored in the refrigerator for subsequent use in ion exchange experiments.

4.1.2 Resin selection and dosing

Amberlite 200c cation exchange resin (CER) was used in all ion exchange experiments. Amberlite 200c was chosen due to its strong affinity for calcium and magnesium. Amberlite 200c is a strong acid cation exchange resin with styrene divinylbenzene copolymer matrix and sulfonic acid functional groups (Rohm and Haas, 1999). Sodium is used as the mobile counter ion in the exchange reactions. The initial resin doses and contact time were chosen from previously unpublished data from Dr. Boyer's research group, which investigated ion exchange treatment of synthetic urine. It was necessary to have a contact time that allowed the CER to uptake the maximum amount of magnesium and calcium from the urine. The previous data showed that removal potential began to level off around 120 min of contact time. The previous experiment examined resin doses from 2 mL/L to 20 mL/L. The desired calcium and magnesium removal was not seen in the 20 mL/L dosed samples. This led to the choice of using a greater range of CER doses that would allow for more calcium and magnesium removal. The final CER doses were 6, 10, 20, 30, and 40 mL/L. Cation exchange resin doses are given as wet resin volumes, meaning that the dry resin needed to be mixed with deionized (DI) water to make a slurry. The resin slurry was then transferred to 10 mL graduated cylinders using disposable plastic droppers until the desired volume of resin was reached. The supernatant liquid in the graduated cylinder was removed from the top of the settled resin. The density of the dry resin was determined by drying and weighing 1 mL of wet resin according to the Standard Method 2540 D. (total suspended solids dried at 103-105°C) (Clesceri et al., 2005).

4.1.3 Batch tests

Batch tests were used to quantify calcium and magnesium uptake by CER. One hundred milliliters of the urine was transferred to 250 mL amber glass bottles. The specified dose of CER was placed in a labeled bottle. Each dose was done in triplicate. The bottles were then transferred to a shaker table which was set to 275 rpm for 120 min. Each sample was then filtered to remove all the resin and any particulate matter. Due to the high ionic strength of the urine, each sample had to be diluted 10× before analysis. The calcium and magnesium concentration for each sample were determined by two different analytical techniques, as discussed in section 4.4.

4.2 Precipitation Experiments in Simulated Hydrolyzed Urine

4.2.1 Calcium- and magnesium-free aged urine

A synthetic urine mixture was prepared to represent aged urine, or urine that has undergone urea hydrolysis. The aged urine mixture was modeled after values found in the literature for aged human urine. The synthetic aged urine was prepared by adding Na_2SO_4, KCl, NH_4Cl, NH_4HCO_3, NaCl, NH_4OH, and NaH_2PO_4 to DI water. The final constituents were modeled after (Udert, 2003a) and can be seen below in Table 4-2. Since the experiments varied the calcium and magnesium concentration, the synthetic aged urine did not include either constituent.

4.2.2 Magnesium and calcium stock solutions

Two stock solutions were made in order to dose the urine with magnesium and calcium. The magnesium solution was made using $MgCl_2 \cdot 6H_2O$ and was 0.1 M in strength. The calcium solution was also made to a strength of 0.1 M and was prepared with $CaCl_2 \cdot 2H_2O$. Both solutions were prepared in DI water and filtered prior to use.

4.2.3 Precipitation experiments

The synthetic aged urine mixture was measured into Erlenmeyer flasks on a stir plate and allowed to reach laboratory temperature before beginning the experiment. Each flask received a measured amount of both the magnesium and calcium stock solutions. The amount each sample received reflected the amount of magnesium and calcium that remained in solution after ion-exchange treatment. There was a sample for each dose of CER used in the fresh urine ion-exchange experiments and one blank. Each dose was done in duplicate. The calcium and magnesium solutions were added at approximately the same time. After these additions, the urine was mixed on medium-high speed for 15 min, to allow for the added magnesium and calcium to form precipitates with the phosphate contained in the aged urine mixture. This time was chosen based on previous research that found almost complete precipitation phosphate minerals in 15 min (Ronteltap et al., 2007). When the mixing was completed, each sample was filtered to remove any solids that had precipitated. The solids that were captured on the filter were dried and weighed according to Standard Method 2540 D. (total suspended solids dried at 103-105°C) (Clesceri et al., 2005). The filtrate was analyzed for magnesium, calcium, phosphate, and nitrogen. Figure 4-2 is a schematic showing a detailed overview of the precipitation experiments.

4.3 Phosphate Dosing Precipitation Experiments

4.3.1 Phosphate-free synthetic aged urine mixtures

Three phosphate-free synthetic urine mixtures were prepared according to (Udert, 2003a) with the elimination of phosphate. One was prepared without calcium and the full magnesium concentration found in urine (magnesium only). Another contained the full amount of calcium but no magnesium (calcium only). The final mixture contained the

entire amount of magnesium and calcium found in urine. For the two mixtures containing calcium, bicarbonate was not added to prevent immediate precipitation of $CaCO_3$. The final concentrations of the three phosphate-free simulated hydrolyzed urine mixtures can be seen below in Table 4-3.

4.3.2 Stock phosphate solution

A 0.1M stock phosphate solution was prepared using NaH_2PO_4 in DI water. The solution was filtered prior to use.
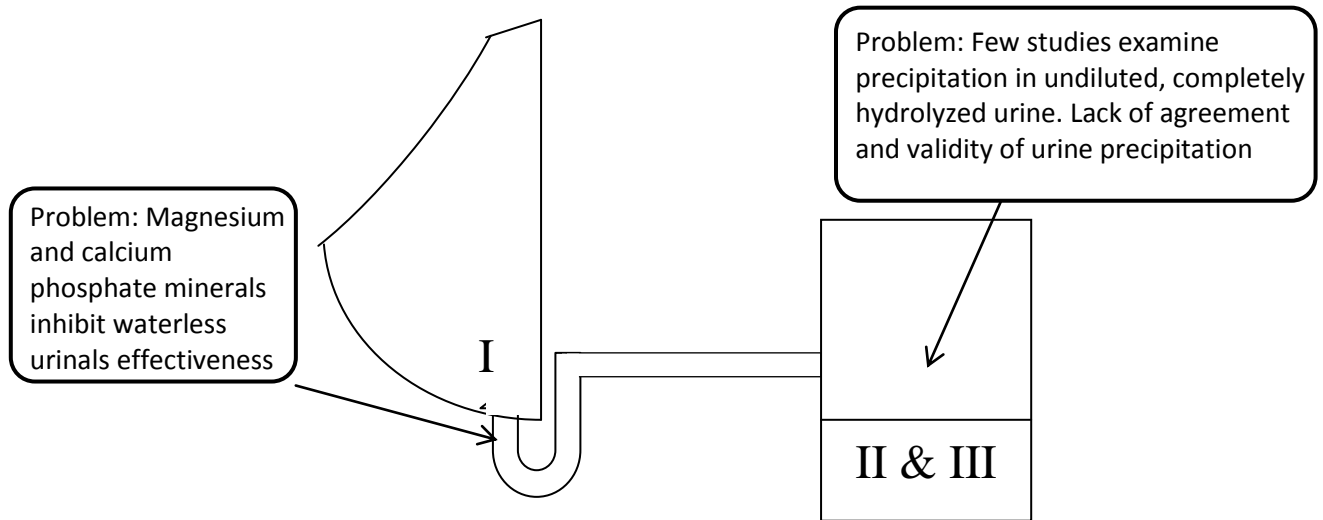
4.3.3 Phosphate dosing experiments

A set of samples of each of the phosphate-free simulated hydrolyzed urines were dosed with varying amounts of the stock phosphate solution. The samples were allowed to mix for 15 min, to allow for the precipitation of phosphate minerals. The samples were then filtered to remove all precipitated solids. The filtrate was analyzed for magnesium and calcium.

4.4 Analytical Methods

All solutions were prepared using ACS grade chemicals and DI water. All filtering was done using a vacuum filter apparatus and 0.45 μm nylon membrane filters. Calcium and magnesium were measured by titration for total hardness and calcium hardness. Total hardness was determined by Standard Method 2340 C. (EDTA titrimetric method) (Clesceri et al., 2005) . The buffer solution was prepared with ammonium chloride, ammonium hydroxide, and magnesium salt of EDTA and stored in a plastic bottle. The pH adjustment was measured on Acumet AP71 pH meter with a pH/ATC probe. The indicator used was a calmagite solution. The standard 0.01 M EDTA titrant was made from reagent grade EDTA and standardized against a standard calcium solution. Analysis for calcium hardness followed Standard Method 3500-Ca B. (EDTA titrimetric

method) (Clesceri et al., 2005). The indicator used was Eriochrome Blue Black R indicator. The pH was adjusted with a sodium hydroxide solution to between pH 12 and 13. The same EDTA titrant was used as in the method for total hardness.

Calcium, magnesium, and ammonium were measured on a Dionex ICS-3000 ion chromatograph (IC) using IonPac CG12A guard and CS12A analytical columns, cation self-regenerating suppressor, 20 mM methanesulfonic acid eluent at 1.0 mL/min, and a 25 µL sample loop. Standard solutions were prepared using calcium chloride, magnesium chloride, and ammonium chloride. Phosphate was also measured on the Dionex ICS-300 ion chromatograph with an IonPac AG22 guard and AS22 analytical column, an anion self-regenerating suppressor, eluent composition of 4.5 mM Na_2CO_3/1.4 mM $NaHCO_3$ (AS22 eluent concentrate, Dionex), eluent flow rate of 1.2 mL/min, and a 25 µL sample loop. The precision of these measurements was monitored by calculating the percent difference between duplicate samples. The calibration check standards were monitored to ensure that they fell within 10% of the known values for accuracy.

Problem: Magnesium and calcium phosphate minerals inhibit waterless urinals effectiveness

Problem: Few studies examine precipitation in undiluted, completely hydrolyzed urine. Lack of agreement and validity of urine precipitation

I

II & III

Experiment	Main Question	Studied Parameters
bl	Can CER remove magnesium and calcium from fresh urine?	- CER dose - Ca/Mg concentration - Composition of fresh urine
II	Will magnesium and calcium removal by CER affect the composition or amount of precipitates formed?	- Composition of fully hydrolyzed urine - Ca/Mg/ PO_4 concentrations - Precipitates formed
III	How does PO_4 concentration affect precipitation?	- Equilibrium models - Ca/Mg/PO_4 concentrations

Figure 4-1.   Overview of lab experiments, main research questions and studied parameters.

Fresh Urine + CER

| 0 mL/L | 6 mL/L | 10 mL/L | 20 mL/L | 30 mL/L | 40 mL/L |

Aged urine containing NH_4 and PO_4

Filtrated analyzed for Ca, PO_4, and Mg

Retentate (calcium-phosphate and magnesium-phosphate minerals) weighed
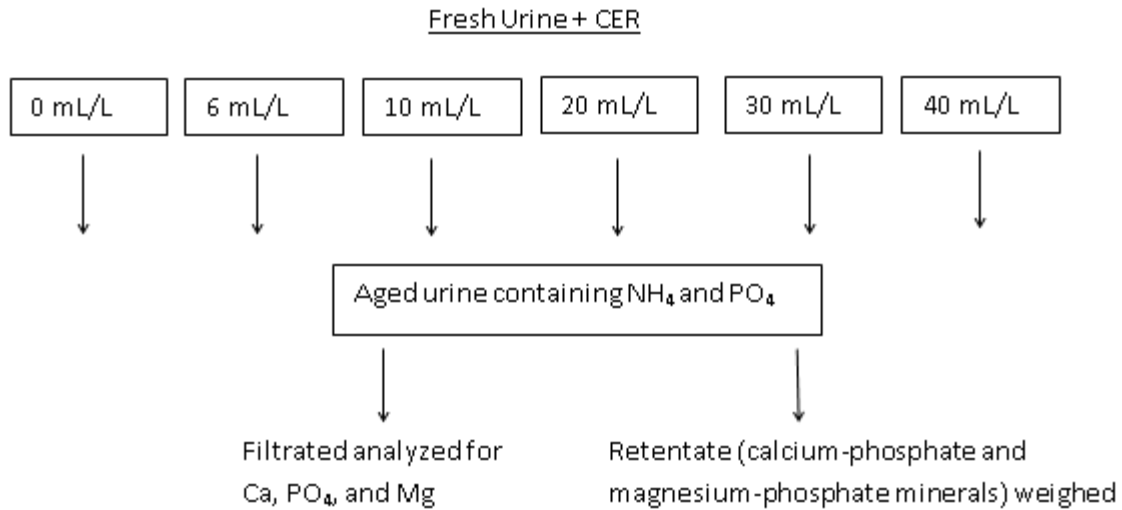
Figure 4-2.   Process schematic for precipitation experiments using synthetic aged urine.

Table 4-1. Chemical concentrations in fresh human urine and the final synthetic fresh urine mixture.

Constituent	Average in Fresh Urine	Final Synthetic Fresh Urine
Urea (mmol-N/L)	550	550
Ca^{2+} (mmol/L)	4.7	4.3
Mg^{2+} (mmol/L)	4.1	3.85
Na^+ (mmol/L)	113	136.9
Cl^- (mmol/L)	107	151
SO_4^{2-} (mmol/L)	15.6	16.1
NH_3 (mmol-N/L)	34.2	37.5
K^+ (mmol/L)	56.3	56.3
PO_4^{3-} (mmol-P/L)	23.9	0
pH	6.2	6.9
Ionic Strength	0.206	0.1997

Note: Average fresh urine data obtained from (Udert et al, 2003) .

Table 4-2. Chemical composition of calcium- and magnesium-free simulated hydrolyzed urine.

Constituent	Synthetic Aged Urine
Urea (mmol-N/L)	0
Ca^{2+} (mmol/L)	0
Mg^{2+} (mmol/L)	0
Na^+ (mmol/L)	106.9
Cl^- (mmol/L)	170
SO_4^{2-} (mmol/L)	16
NH_3 (mmol-N/L)	288
K^+ (mmol/L)	46
PO_4^{3-} (mmol-P/L)	23.9
NH_4^+ (mmol-N/L)	339
HCO_3^{2-} (mmol/L)	266
pH[a]	9.069
Ionic Strength[a]	0.5665

[a]: Calculated by Visual MINTEQ

Table 4-3. Chemical composition of synthetic phosphate-free simulated hydrolyzed urine solutions.

Constituent	Phosphate-free (both Ca and Mg)	Calcium-Only (phosphate-free)	Magnesium- Only (phosphate-free)
Urea (mmol-N/L)	0	0	0
Ca^{2+} (mmol/L)	4.7	4.7	0
Mg^{2+} (mmol/L)	4.1	0	4.1
Na^+ (mmol/L)	83	83	83
Cl^- (mmol/L)	453.6	445.4	178.2
SO_4^{2-} (mmol/L)	16	16	16
NH_3 (mmol-N/L)	288	288	288
K^+ (mmol/L)	46	46	46
HCO_3^{2-}(mmol/L)	0	0	266
PO_4^{3-} (mmol-P/L)	0		
NH_4^+(mmol-N/L)	339	339	339
pH[a]	9.260	9.2	9.1
Ionic Strength[a]	0.4752	0.4662	0.5263

[a]: Calculated by Visual MINTEQ

CHAPTER 5
RESULTS

5.1 Ion Exchange Experiments using Fresh Urine

Magnesium and calcium concentrations in the synthetic fresh urine following the batch ion-exchange experiments were measured by both ion chromatography and hardness titrations. The two concentrations as a function of CER dose can be seen in Figures 5-1 and 5-2. The values between the two techniques are similar and the concentration can be seen to decrease as the CER dose increased.

5.2 Precipitation Experiments in Simulated Hydrolyzed Urine

5.2.1 Concentrations of calcium and magnesium added

The amount of calcium and magnesium added to the synthetic aged urine was dependent on the results of the ion exchange experiments using fresh urine. The removals found for each CER dose were averaged to find the concentration of magnesium and calcium that reflected what would remain after cation exchange treatment. Due to the resins higher affinity for calcium, the range of calcium added was much wider than that of magnesium. One sample was meant to represent no cation exchange treatment and received a dose of 4.7 mmol/L calcium and 4.1 mmol/L magnesium. A blank sample without calcium or magnesium addition was also used. The entire range of added concentrations can be seen in Table 5-1.

5.2.2 Precipitation of calcium, magnesium, and phosphate

The amount of calcium that remained in the aged urine after the removal of the precipitate ranged from 0.67 mmol/L, in the samples representing no cation exchange, to 0.39 mmol/L, in the samples dosed with 40 mL/L of CER. Levels of magnesium in the filtered samples did not follow a trend with resin dosage but remained around an

average of 0.68 mmol/L. Phosphate showed a ranged in concentration from 16 mmol/L to 19 mmol/L. Measurement error could be an issue due to the dilution required for phosphate analysis on the ion chromotograph. The remaining amount of phosphate followed a good overall trend, apart from sample A, which has a higher concentration than sample B, contrary to what was expected. Figure 5-3 shows the initial amount of each element added to each sample and the concentrations remaining in the filtered samples.

5.2.3 Mass of precipitate

At every CER dose precipitation was observed almost immediately. Table 5-2, shows the dry mass of each precipitate collected for each resin dose. The decrease in mass is also plotted against CER dose and can be seen in Figure 5-4.

5.3 Phosphate Dosing Precipitation Experiments

The two graphs below show the amount of HAP and struvite precipitated at each dose of phosphate. Figure 5-5, depicts HAP precipitation both with and without magnesium present. HAP, though it may not be the only calcium phosphate mineral present, is used as a benchmark because it has similar phosphate to calcium ratios to the other calcium phosphate minerals and it will be the only mineral present at equilibrium. Further discussion of this issue can be found in sections 4.7 and 4.8. Figure 5-6, shows the struvite that precipitated with the added phosphorus, one data set shows the precipitation in the presence of calcium, the other in the calcium-free urine. The precipitation of calcium in the presence of magnesium is lower than in the magnesium-free urine at lower doses of phosphate. This difference could signal that when phosphate is the limiting factor in urine precipitation of struvite precedes HAP formation.
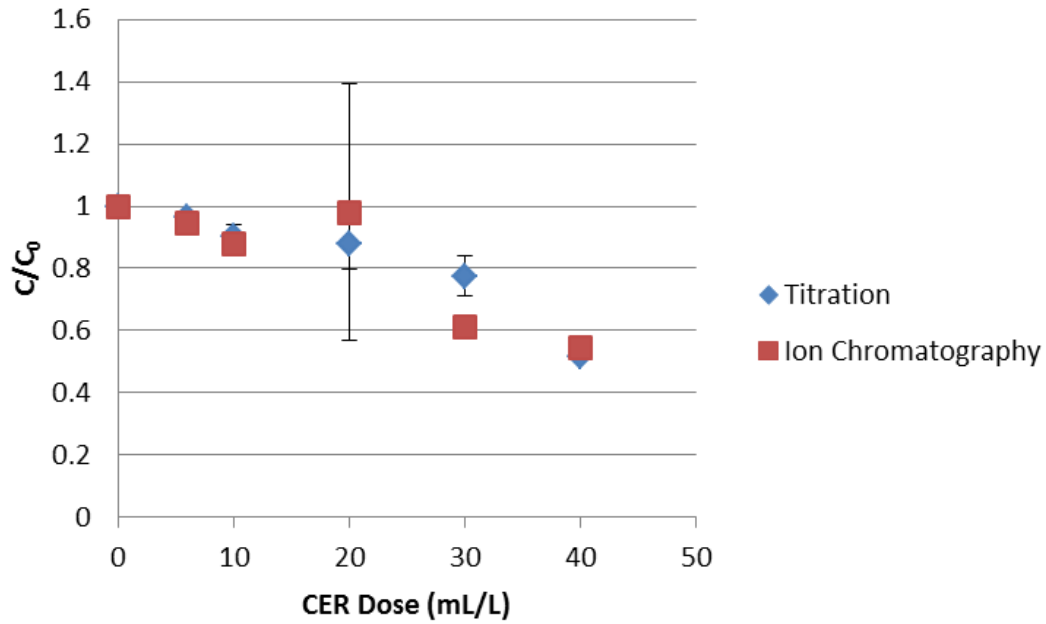
Figure 5-1. Jar test results showing magnesium concentration as a function of resin dose for both detection methods (C_0 = 3.85 mmol/L).
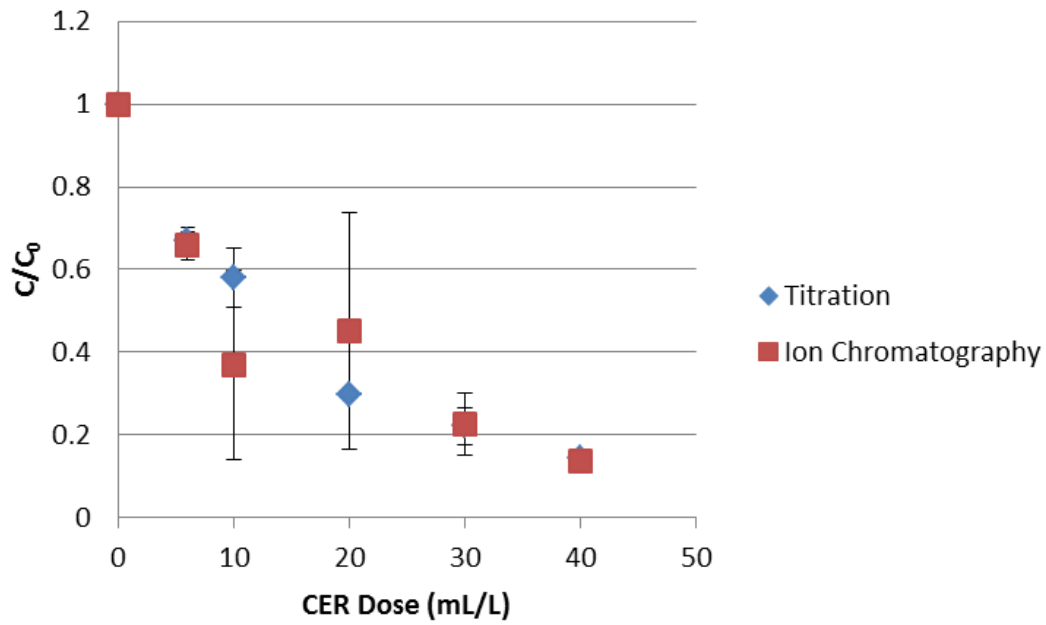

Figure 5-2. Jar test results showing calcium concentration as a function of resin dose for both detection methods (C_0 = 4.3 mmol/L).
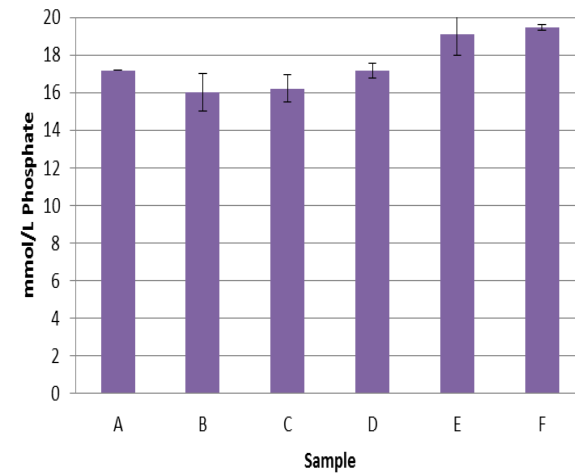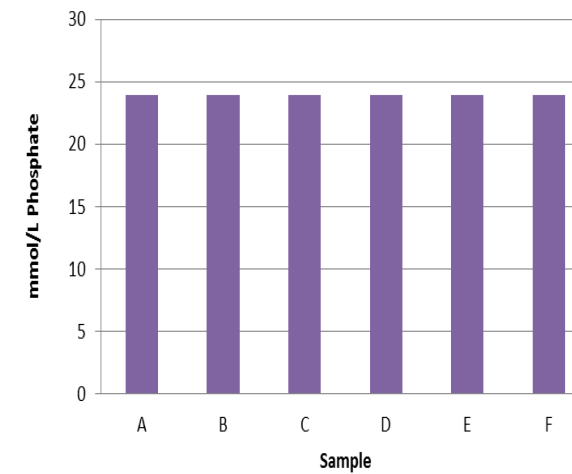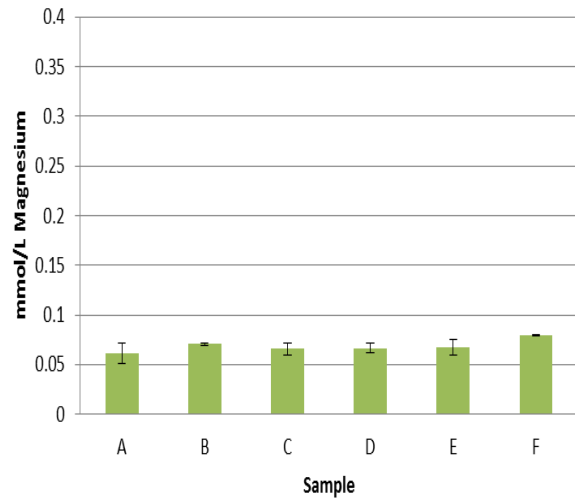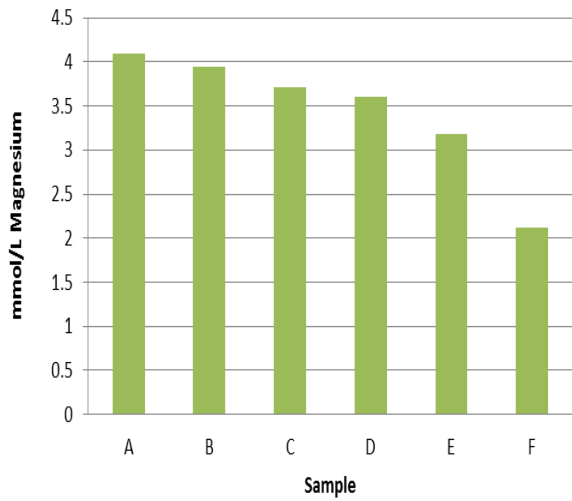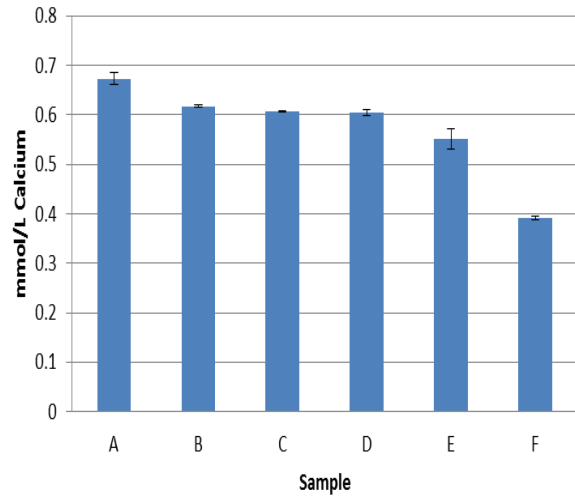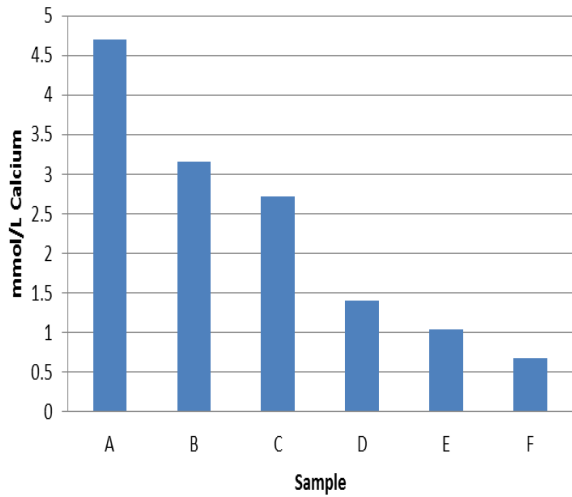
Figure 5-3.   Graphs showing amount of calcium, magnesium, and phosphate initially added to each sample (on left) and remaining in each sample after precipitation (on right). Table 5-1 provides description of samples.
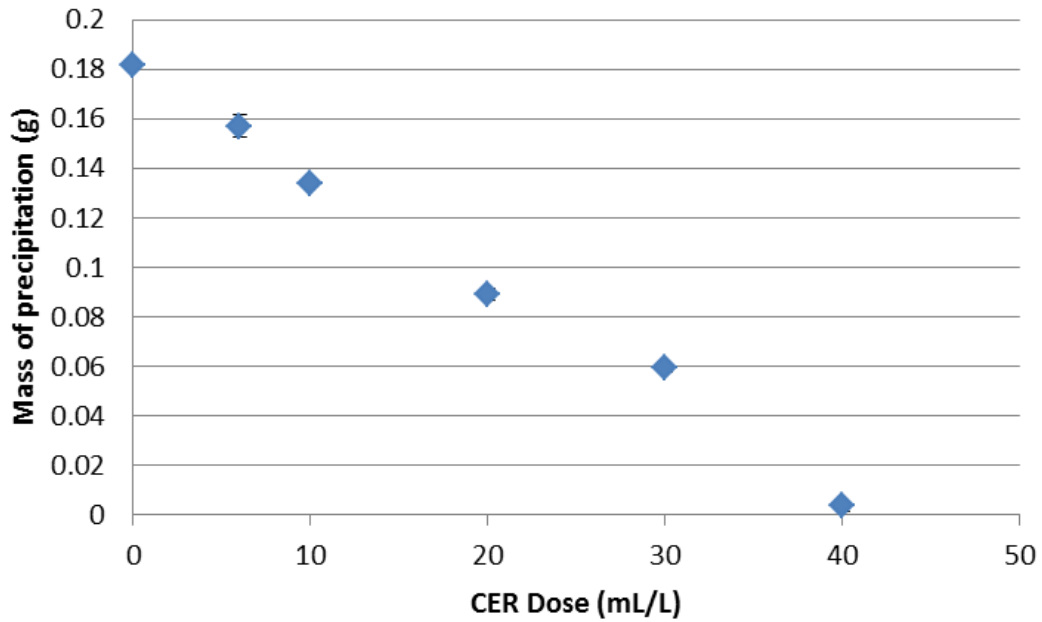
Figure 5-4.   Graph depicting the decreasing mass of precipitate collected as CER dose increases.
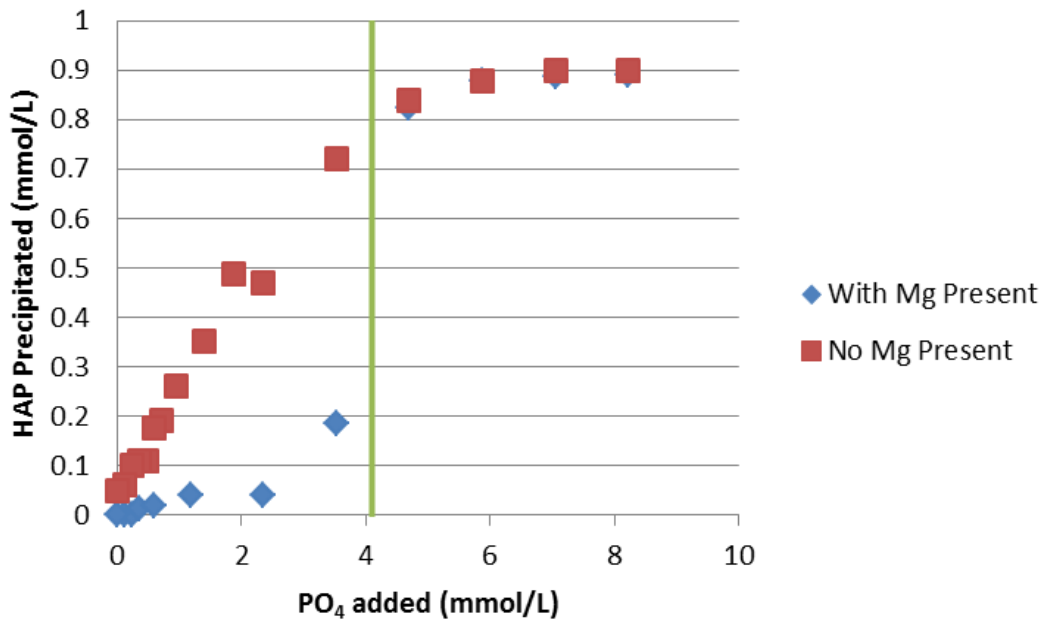
Figure 5-5.   Amount of HAP formed in simulated hydroloyzed urine at specific doses of phosphate with and without magnesium present. The vertical line represents the dose of phosphate that satisfies complete struvite precipitation with magnesium.
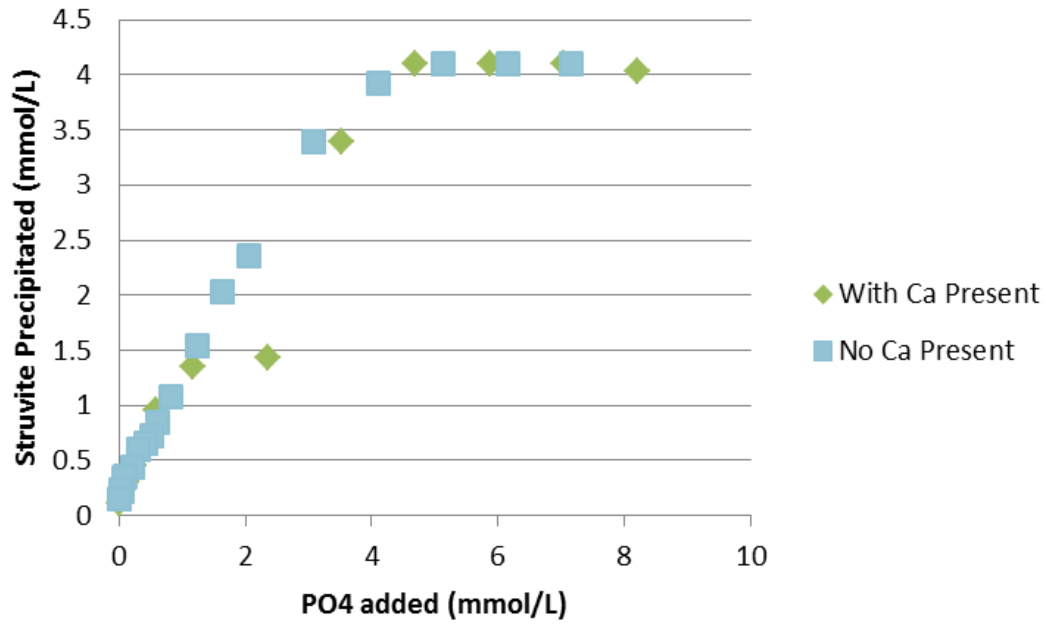
Figure 5-6. Amount of struvite formed in fully hydrolyzed urine at varying phosphate doses with and without calcium present.

Table 5-1. Amount of calcium and magnesium added to samples to represent treatment at various CER doses.

| Sample	A	B	C	D	E	F
CER dose (mL/L)	0	6	10	20	30	40
Calcium added (mmol/L)	4.7	3.15	2.72	1.4	1.044	0.676
Magnesium added (mmol/L)	4.1	3.95	3.71	3.6	3.18	2.12

Table 5-2. Mass of dried precipitate collected after filtration of samples.

Sample	Precipitate collected (g)
A	0.1818
B	0.15705
C	0.13395
D	0.08885
E	0.0596
F	0.00345

CHAPTER 6
DISCUSSION

6.1 Accuracy and Comparison of Ion Chromatography (IC) and Titration Measuring Techniques

The IC data appears accurate for most values, however, a few values deviated greatly from the overall trend (Figures 5-1 and 5-2). This is a result of the fact that the IC can have instrument error that can sometimes lead to results that are erroneously high or not displayed at all. Figures 5-1 and 5-2 show that while there is slight variability among the IC and titration methods for measurements of calcium and magnesium, both are able to give relatively reliable values. All subsequent data are based on titration methods because of the error associated with the necessary dilutions for the IC.

6.2 Calcium and Magnesium Cation Exchange Isotherms in Fresh Urine

Treatment with cation exchange resin was able to achieve removal of both magnesium and calcium from the synthetic fresh urine. However, the removal of calcium was much greater than that of magnesium. The highest dosage of resin was able to remove about 90% of the calcium but only about 40% of the magnesium.

An isotherm for the CER was determined by graphing the concentration of calcium and magnesium on the CER phase as a function of the concentration of calcium and magnesium remaining in solution (Figure 6-1). The concentration on the CER was found by subtracting the concentration left in solution from the initial concentration divided by the mass of dry resin. The isotherms further highlight the preference of the CER for calcium. As the calcium concentration in the solution increase, the amount on the CER surface also increases. For magnesium however, the concentration on the resin remains steady even as the magnesium in solution increases.

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Calculations of the exchange capacity at each CER dose and the equivalent magnesium and calcium removed by the resin showed that the CER was between 17% and 33% saturated with magnesium and calcium ions. This low saturation is most likely due to the high competition from other ions like sodium and potassium. At a resin dose of 6 mL/L there is about 13x more sodium and 5x more potassium in the urine than exchange sites available on the CER. The fact that the removal of magnesium and calcium was still achieved with such competition highlights CER's selectivity for magnesium and calcium over other monovalent ions.

6.3 Struvite and HAP Saturation Index Calculations

The next step was to see whether or not the removal by ion exchange would change the amount of HAP and struvite that would precipitate in the system. A common calculation used to determine whether or not mineral precipitation will occur is the saturation index (SI). From Essington (2004) it is known that:

$$SI = \log(IAP/K_{sp}) \tag{5-1}$$

Where K_{sp} is the solubility product and IAP is the ion activity product. If the SI is positive, the solution is supersaturated and the mineral with will precipitate, while if the SI is negative the solution is undersaturated and no precipitation will occur (Essington, 2004). For HAP and struvite, the following equations govern SI calculations:

$$Struvite \leftrightarrow Mg^{2+} + NH_4^+ + PO_4^{3-} \qquad pK_{sp}= 13.15 \tag{5-2}$$

$$IAP= \gamma_{Mg2+}[Mg^{2+}]\gamma_{NH4+}[NH_4^+]\gamma_{PO43-}[PO_4^{3-}] \tag{5-3}$$

$$HAP \leftrightarrow 5Ca^{2+} + 3PO_4^{3-} + H^+ \qquad pK_{sp}= 57.5 \tag{5-4}$$

$$IAP= \gamma_{Ca2+}[Ca^{2+}]^5 \gamma_{PO43-}[PO_4^{3-}]^3\gamma_{H+}[H^+] \tag{5-5}$$

For accuracy, the SI values were determined using Visual MINTEQ, version 3.0 (Visual MINTEQ, 2011), a computer modeling software that allows for specific calculations of activities, SI, and IAP by inputting the chemical composition of a solution. Since precipitation of urine is triggered by urea hydrolysis (Udert, 2003b), the constituents entered into Visual MINTEQ were that of the simulated hydrolyzed urine, the calcium and magnesium concentrations were then varied to represent the amount remaining after each CER dose. If any of the samples' magnesium or calcium concentrations resulted in a negative SI value for either HAP or struvite then it could be assumed that precipitation could be prevented by that CER dose.

The calculated SI for HAP and struvite for each sample can be seen in Figure 6-2. For both minerals, the SI are positive in all IX-treated samples, indicating that precipitation could be possible. However, a positive SI only indicates that precipitation is thermodynamically favorable and does not give any indication of how much precipitation can be expected and at what rate. For these reasons, the following experiments were meant to quantify the precipitation of minerals .The SI of both minerals in sample A, representing non-IX treated urine are very similar to what Udert (2003c) found in undiluted hydrolyzed urine. This agreement leads us to assume that the model can produce accurate SI values for HAP and struvite in urine and gives confidence in the calculated values of the other samples.

6.4 Precipitation Reduction in Cation Exchange Treated Urine

The goal of this experiment was to measure and quantify the difference in the HAP and struvite formation at different resin doses. The SI calculations in the previous section showed that precipitation would occur at even the highest CER dose, but was unable to show the amount that would form. The data of the remaining magnesium,

calcium, and phosphate in the filtrate shown in Section 5.2.1 was compared to the added calcium and magnesium stock solutions as well as the concentration of phosphate in the aged urine solution. By subtracting the amount found in the filtrate from the initial concentrations, the fraction of magnesium, calcium, and phosphate that precipitated out during the mixing period was estimated. Below in Figure 6-3, the fraction of each element that was precipitated is shown for each resin dose.

Figure 6-1 shows that the fraction of calcium precipitate is most affected by the change in CER dose. With no ion exchange treatment, about 86% of the calcium is precipitated and at the highest CER dose of 40 mL/L that percentage is reduced to 42%. The precipitation of magnesium is less affected by the change in resin dose and remains almost constant with 98% precipitated. The precipitation of phosphate, which is affected by both HAP and struvite formation, is dependent on the levels of both magnesium and calcium. The reduction in calcium precipitation, also leads to a reduction in phosphate precipitation from about 33% to 19%.

6.5 Mass of Struvite and HAP Precipitates

The measured concentration of magnesium and calcium precipitated were used to determine the theoretical amount of struvite and HAP precipitated. Struvite was determined by the 1:1 stoichiometric molar ratio between magnesium and struvite. Moles of HAP formed was calculated from the 1:5 ratio of HAP to calcium. These calculations are based on the fact that in undiluted urine HAP and struvite are the main precipitates found (Udert, 2003c) and that all of the calcium and magnesium precipitated can be assumed to be assimilated entirely into HAP and struvite, respectively. Once the molar concentrations of struvite and HAP were found, they were adjusted by the sample size and molecular weights to estimate the theoretical mass of

each solid formed in each sample. Figure 6-4 shows that the majority of the mass of precipitate can be contributed to struvite. In the sample that received no IX treatment the mass fraction of struvite is 0.71. These values are in agreement with Udert (2003c) who determined that in undiluted, aged urine struvite represents approximately 68% of the mass of precipitation, while HAP accounted for the additional 32%. With increasing CER dose, the mass fraction of struvite increases, with about 95% of the mass at the highest resin dose being struvite.

The much higher mass fraction of struvite hinders the effectiveness of cation exchange to reduce the precipitation potential of urine. The struvite formation is a result of the remaining magnesium because the CER shows greater selectivity for calcium. The highest CER dose effectively removed around 90% of the calcium and 40% of magnesium in the fresh urine. The calculations indicate the mass of precipitate would be about 38% of non-ion-exchange treated urine. Since the remaining mass of precipitate is almost purely struvite, higher magnesium removal would most likely greatly improve precipitation reduction. Finding an alternative cation exchange resin that has a higher affinity for magnesium could provide a way to lower the amount of struvite precipitated. Levanmao et al. (1994) found that natural zeolite Na-X provided 52.5% magnesium removal from solution at room temperature and 69.7% removal at 45°C. The average temperature of fresh urine is about 37°C which would allow for a substantially higher amount of magnesium removal from urine than shown by the Amberlite 200c.

Treatment with CER may not be able to drastically reduce the precipitation formed in hydrolyzed urine, however, it may provide a way to further another technology used in

urine treatment. The idea of controlled precipitation, collection, and use of as a fertilizer of struvite in source-separated urine has been suggested for nutrient recycling (Harada et al., 2006; Ronteltap et al., 2007; Wilsenach et al., 2007b; Etter et al., 2011). However, most studies have determined that precipitation of pure struvite would require the addition of both magnesium and phosphate to fully utilize the nutrients in urine at a stoichiometric ratio (Larsen and Gujer, 1996; Kabdasli et al., 2006). Furthermore, Hao et al. (2008) determined that the presence of calcium ions inhibits precipitation of pure struvite. Removal of calcium prior to urea hydrolysis would lower the phosphate lost to HAP precipitation and increase the phosphate concentration in the source separated urine allowing for a higher natural struvite precipitation and reduction of needed phosphate addition.

6.6 Comparison of Calculated and Measured Phosphate Values

In the above calculations, the amounts of struvite and HAP precipitated were determined solely on measured magnesium and calcium concentrations; the phosphate precipitated was assumed to be equal to the stoichiometric phosphate to calcium and phosphate to magnesium ratios found in HAP and struvite, respectively. The amount of phosphate precipitated based on these ratios was compared to the measured amount of phosphate precipitated in the sample as can be seen below in Figure 6-5.

The measured amount of phosphate precipitated is greater than that calculated based on stoichiometric ratios for all samples, except A, which as previously mentioned, probably contained some experimental error. This difference could indicate the presence of additional phosphate minerals, or the formation of other magnesium or calcium phosphate precipitates besides HAP and struvite. Both amorphous calcium phosphate (ACP) and octacalcium phosphate (OCP) are known precursors to HAP in

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urine precipitation, both are calcium phosphate minerals that incorporate a higher amount of phosphate. Their presence could cause the equilibrium amount of phosphate precipitated to be less than measured.

6.7 Measured Mass vs. Theoretical Mass

The theoretical mass of HAP and struvite discussed in the previous section can be thought of as the "wet mass" of the solids because the calculations used the hydrated molecular weight of struvite. The actual measured mass of the collected solids can be considered the "dry mass" because the samples had been dehydrated by Standard Methods 2540 D. The same calculations used in section 4.5 to determine the amount of precipitates based on the stoichiometric ratios to the measured calcium and magnesium were used to determine the "calculated dry mass" for comparison to the collected solids' mass. Figure 6-6 shows this calculated dry mass as well as the mass of the collected solids. There is good agreement between to two data sets in the low CER dosage samples, but at the higher resin doses, the mass of collected solids is lower than what would be expected from the amount of calcium and magnesium that precipitated out of solution. The reason for the difference in masses at higher resin doses is not known.

Calculations made to determine the mass fractions of struvite and HAP found in the dry solids can be compared to the collected precipitate mass, as shown below in Figure 6-7. This graph is a version of Figure 6-4 in Section 6.5 but uses the dehydrated masses of struvite and HAP. The figure highlights the drastic reduction in struvite weight and the accuracy of the mass of solids collected at lower CER doses.

6.8 Comparison of Measured and Calculated Precipitation Results to Modeled Results

Visual MINTEQ was used to compare the experimental results to the modeled equilibrium results. Figures 6-8 – 6-10 shows the modeled amount of magnesium, calcium, and phosphate precipitated compared to the amount measured in the experiment. The results and model agree very well for magnesium, nearly 100% being precipitated at every resin dose. This tells us that precipitation of struvite in urine reaches equilibrium very quickly, with the 15 minute mixing time and that further storage will not change magnesium concentrations.

The results for calcium, however, do not agree as well. The results showed, promisingly, that at the highest CER dose that only 40% of the calcium will be incorporated into solids. However, the model shows that at equilibrium a majority of the calcium will precipitate. The amount precipitated will be different at each CER dose, due to the high removal of calcium, but as the model suggests that at equilibrium the amount incorporated into solids remains unchanged by CER treatment. This disagreement suggests that HAP formation did not reach equilibrium within the mixing time, which was based on research of struvite precipitation only (Ronteltap et al., 2007). Further experiments should be conducted with a longer mixing time to see if calcium precipitation is reduced at all or if the Visual MINTEQ predications are accurate. Udert (2003b) showed that after 4.5 h of urea hydrolysis only 70% of calcium was precipitated but was precipitated as OCP. Due to the incomplete urea hydrolysis, the pH was about 8.9. House (1999) determined that in solutions with a pH above 9 (as in fully hydrolyzed urine) OCP is not a precursor to HAP but instead ACP is converted directly into HAP. This suggests that ACP is most likely present in the experimental precipitates Liu et al.

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(2001) found that at 25°C ACP is converted into HAP after 24 h. This suggests that as the urea is being hydrolyzed (and pH is below 9) OCP appears as the first calcium phosphate mineral, as urea hydrolysis is complete (and pH is increased above 9) ACP appears and both are transformed slowly into HAP.

The model predicted that phosphate precipitated at equilibrium would be less than measured during the experiments. This most likely can be attributed to measurement error and does not indicate any change in precipitate composition. However, analysis of the solids could provide insight to whether or not any additional phosphate solids were formed.

Figures 6-11 and 6-12 show the amounts of struvite and HAP formed at each resin dose calculated from the measured calcium and magnesium concentrations and the Visual MINTEQ model. The results of HAP precipitated vary between the model and the calculate values. However, these figures highlight the decrease in both minerals, particularly HAP with CER treatment.
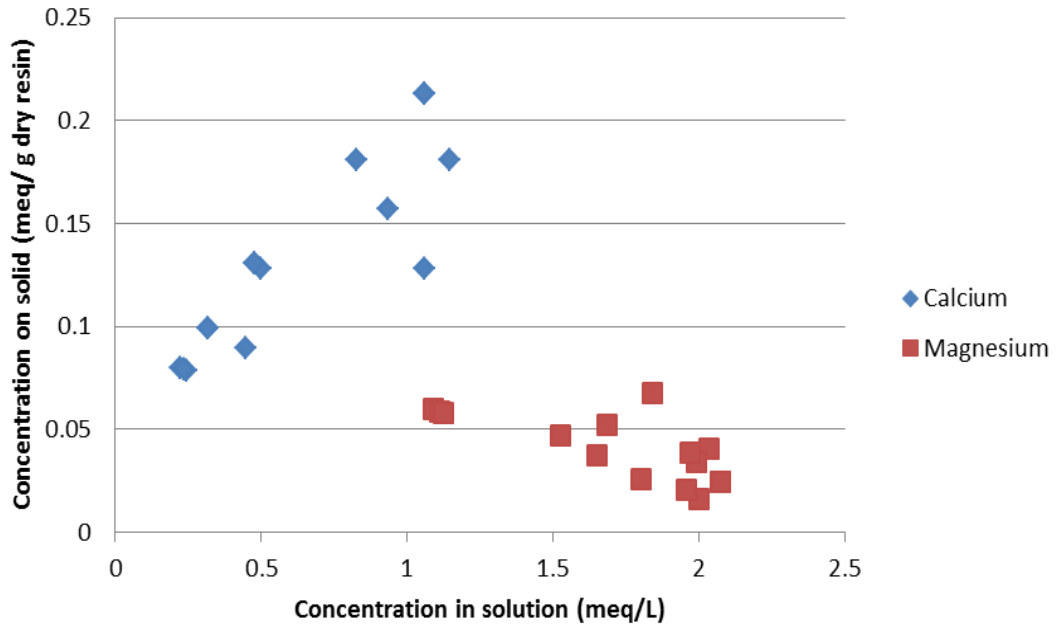
Figure 6-1. Isotherm for magnesium and calcium removal as measured by titrations.
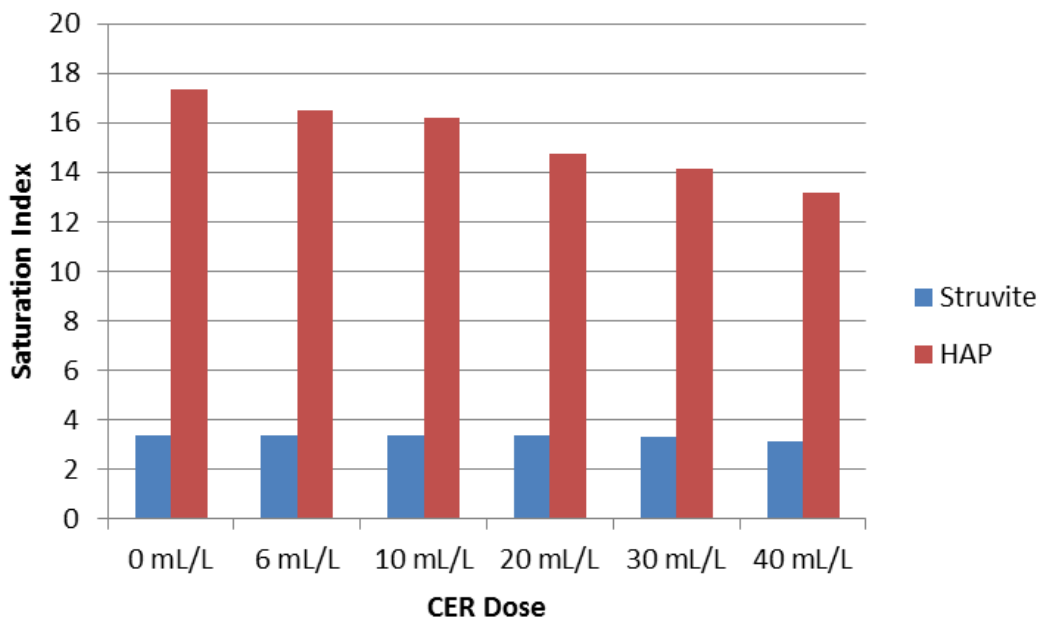

Figure 6-2. Calculated saturation index values for HAP and struvite in hydrolyzed urine for various CER dosages. Table 5-1 gives a description of the samples.
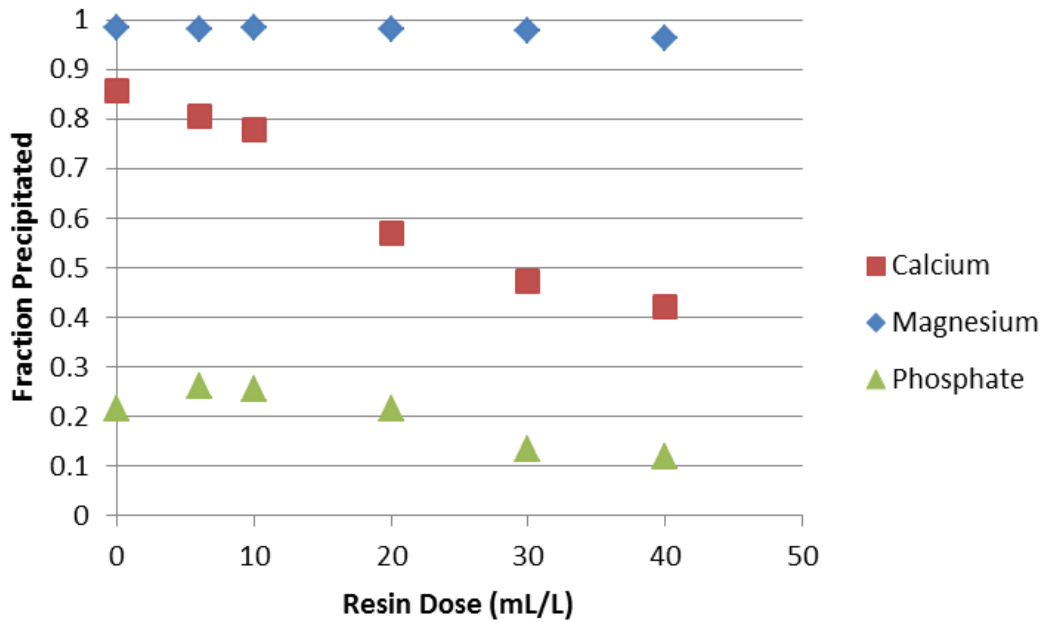
Figure 6-3.   Fractions of phosphate, magnesium and calcium precipitated in each
sample after cation exchange treatment and mixing.

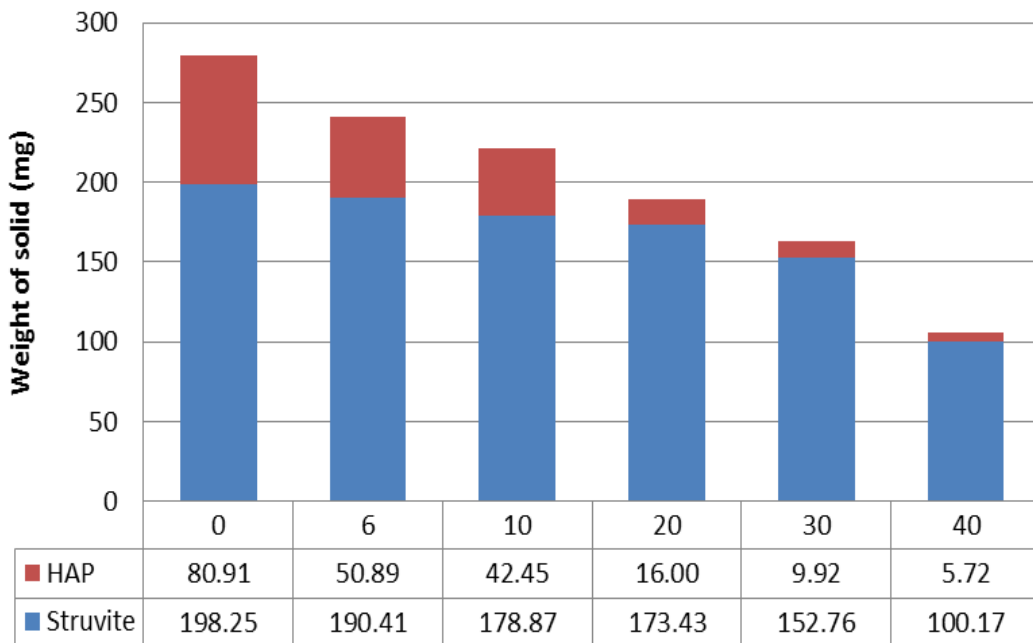|	0	6	10	20	30	40
■ HAP	80.91	50.89	42.45	16.00	9.92	5.72
■ Struvite	198.25	190.41	178.87	173.43	152.76	100.17

Figure 6-4.   Mass fraction of solids expected to form in hydrolyzed urine based on
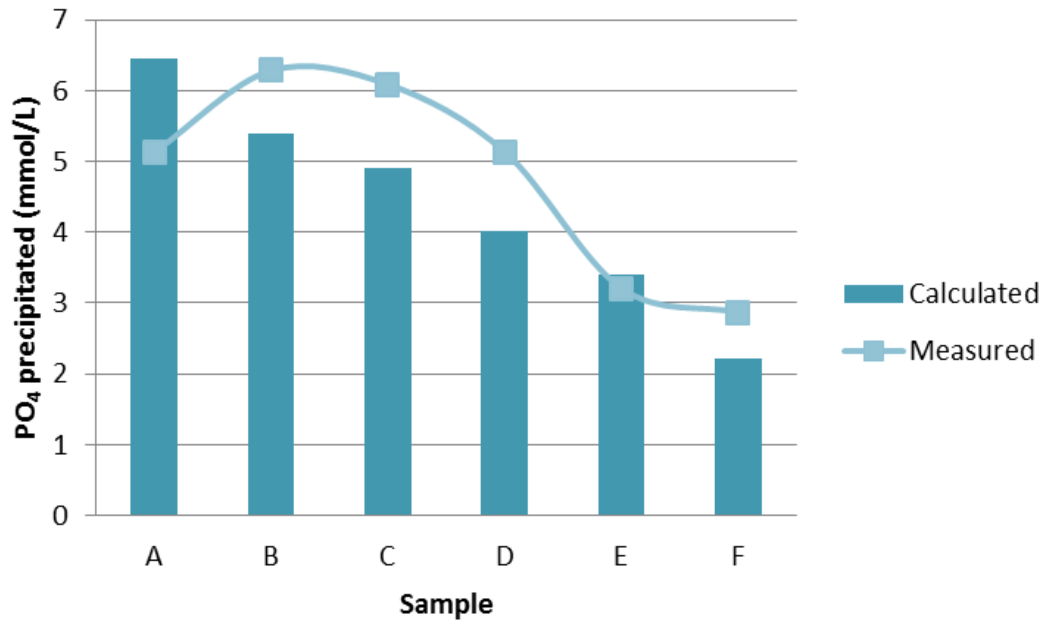magnesium and calcium measurements.

Figure 6-5.   Phosphate precipitated in fully hydrolyzed urine as measured by ion chromatography and determined from stoichiometric ratios with measured magnesium and calcium.
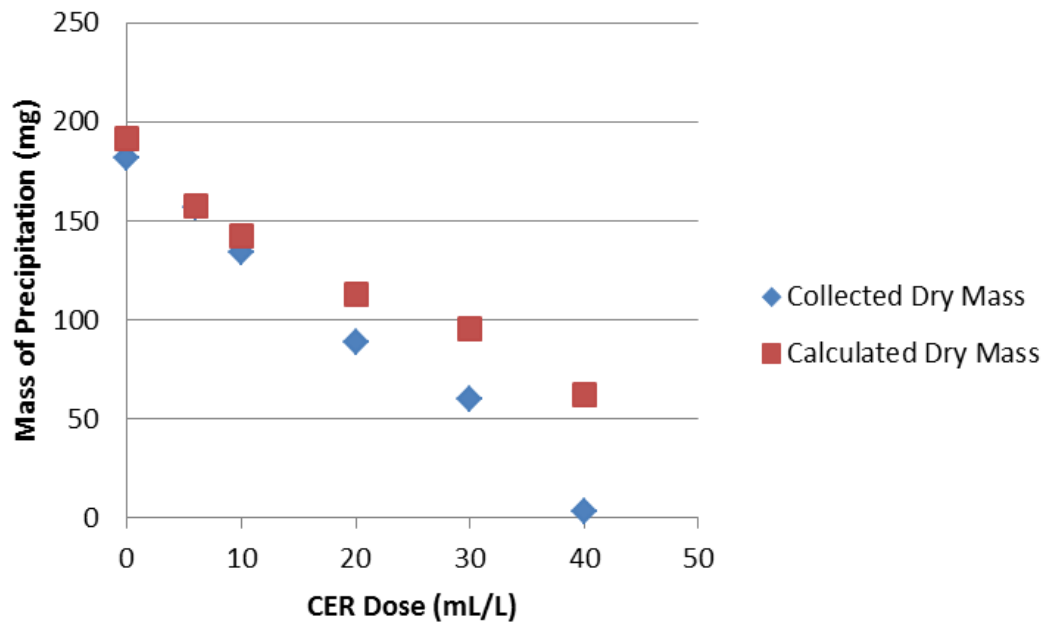

Figure 6-6.   Collected and calculated mass of dry precipitates for each CER dose.

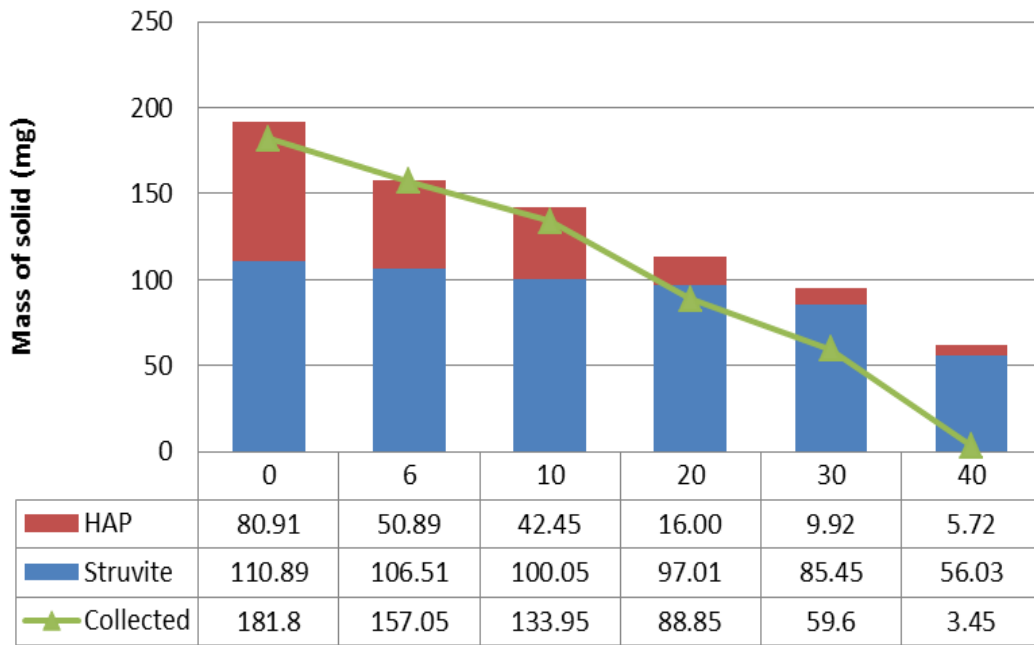|	0	6	10	20	30	40
■ HAP	80.91	50.89	42.45	16.00	9.92	5.72
■ Struvite	110.89	106.51	100.05	97.01	85.45	56.03
▲ Collected	181.8	157.05	133.95	88.85	59.6	3.45

Figure 6-7.   Mass fractions of dry solids expected compared to collected dry solids' mass at each CER dose.
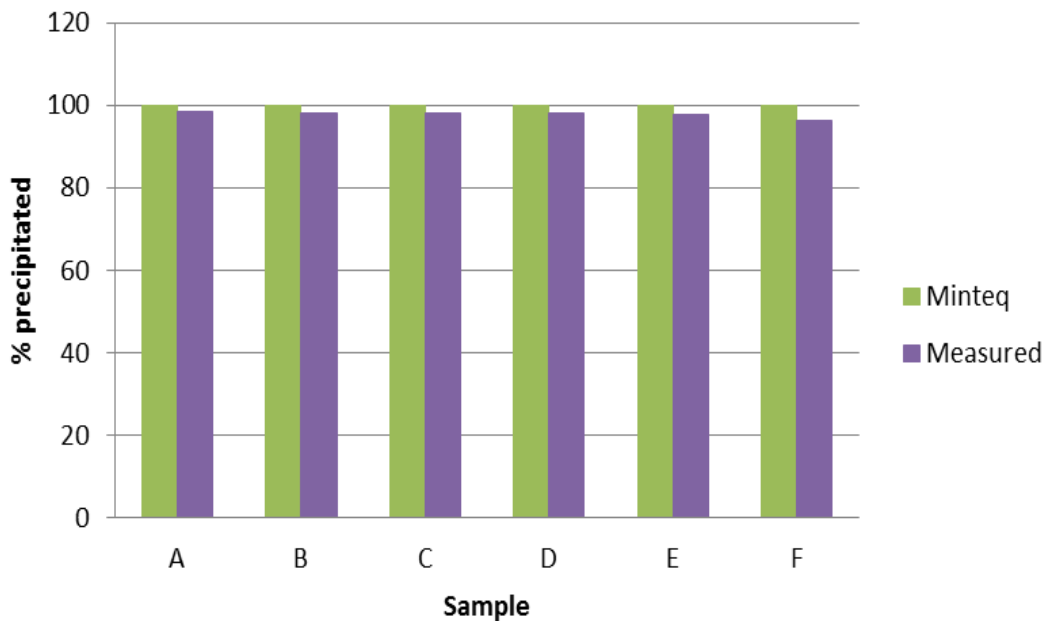

Figure 6-8.   Measured and modeled percent of magnesium precipitated in ion-exchange treated, simulated hydrolyzed urine.
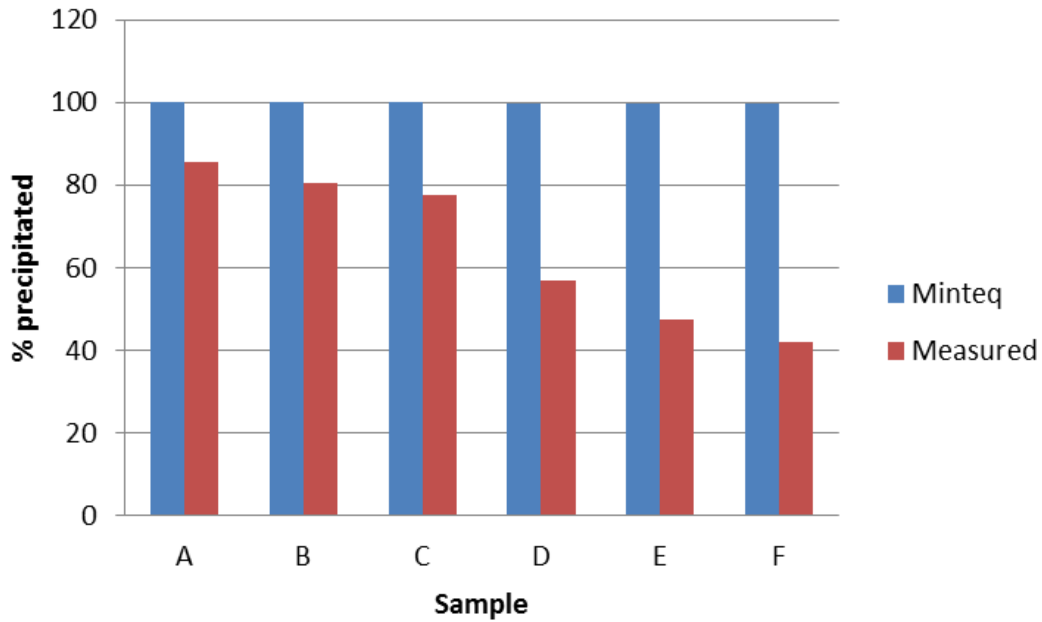
Figure 6-9.   Measured and modeled percent of calcium precipitated in ion-exchange treated, simulated hydrolyzed urine.
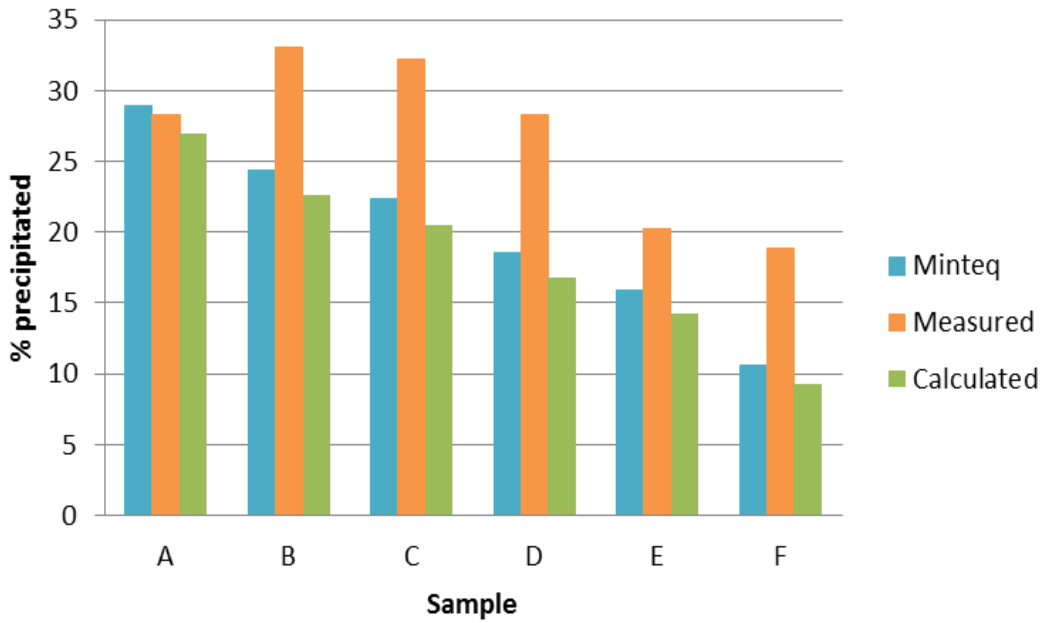

Figure 6-10. Measured and modeled percent of phosphate precipitated in ion-exchange treated, simulated hydrolyzed urine.
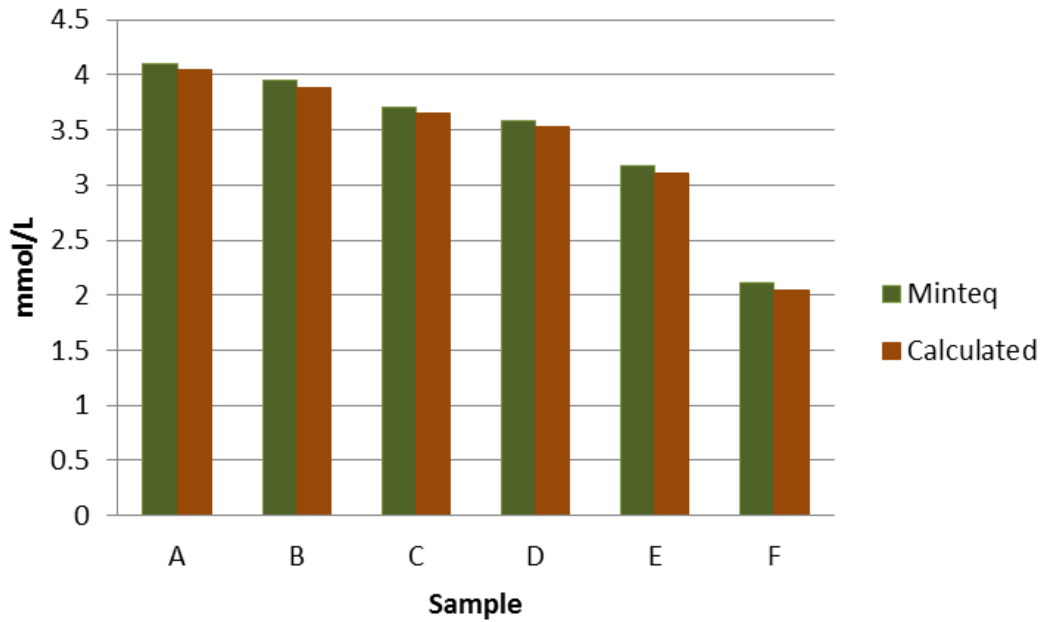
Figure 6-11. Measured and modeled concentrations of struvite precipitated in ion-exchange treated, simulated hydrolyzed urine.
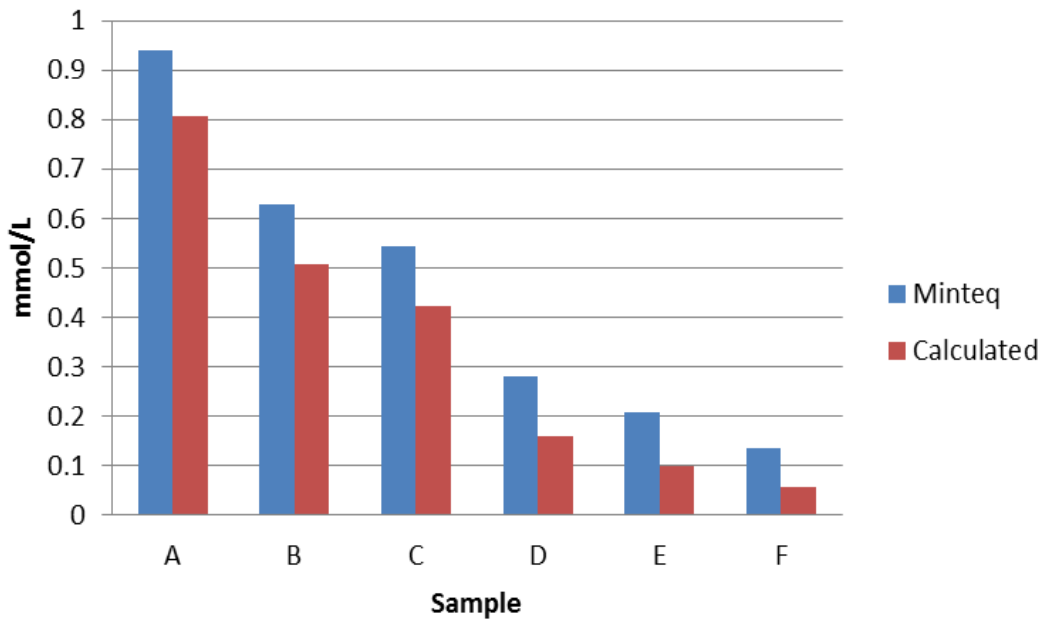

Figure 6-12. Measured and modeled concentrations of HAP precipitated in ion-exchange treated, simulated hydrolyzed urine.

CHAPTER 7
CONCLUSIONS AND FUTURE WORK

Though urine separation can provide many benefits to the environment, its widespread use and success is limited by the usability and operational issues of separation units. Many researches are attempting to quantify the main problems and provide solutions that will promote user acceptance. Economic feasibility, integration into the existing infrastructure, and urine taboos currently hinder this goal. Treatment options for source separated urine are numerous. Nutrient recovery is one of the most desirable goals for urine treatment and one technology in particular, struvite precipitation, has been studied extensively. Although researchers have attempted to optimize the precipitation process in the laboratory, improvement in design of full-scale units is needed before widespread use is possible.

Experiments showed that CER was able to remove both magnesium and calcium from fresh urine. Calcium was preferentially removed, with about 90% removal at the highest resin dose. Magnesium removal was less effective with only 50% removal at the highest resin dose. Subsequent experiments using simulated hydrolyzed urine showed that ion-exchange treatment of urine could provide a reduction of the two most problematic minerals: HAP and struvite. Calculated results indicated a 70% reduction in the mass of precipitates formed at the highest resin dose. An equilibrium model determined that at all CER doses all magnesium and calcium would be precipitated but, due to the removal seen by CER, mass of precipitates formed would decrease.

Though ion-exchange treatment may not be able to prevent problematic precipitation in urine separating systems, it may be useful as a pretreatment to nutrient recovery in urine, specifically struvite precipitation. CER reduces the phosphate bound

in precipitates lost in pipes, traps, and storage units, allowing for higher recovery rates in precipitation units. It also creates a favorable magnesium to calcium ratio for struvite formation, enabling a more valuable product.

Further research into the removal of magnesium and calcium from urine by other cation exchange resins could potentially show an even further reduction of mineral precipitates, especially if there is preferential removal of magnesium. Research on the impact of ion exchange treatment of urine as a pretreatment to struvite precipitation is needed to determine if calcium removal has a significant effect on the recoverable struvite. If calcium removal is determined to be useful, a resin with an even higher calcium preference should be studied. Alternatively, anion exchange resins could be used as a way of collecting and recovering phosphate before spontaneous precipitation occurs. This could eliminate not only the problematic clogging of units but also benefit nutrient recovery.

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BIOGRAPHICAL SKETCH

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