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TECHNOLOGICAL INSTITUTE

EVANSTON, ILLINOIS

Final Report

to the

Commission on Environmental Hygiene
of the
Armed Forces Edpidemiological Board

U.S. Army Medical Research and Development Command

"Continuous Potable Water Supply for Fallout Shelters and Other Isolated Sites"

Contract No. DA-49-193-MD-2316

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ABSTRACT - SUMMARY

In the manned space program, a good deal of effort has been devoted to developing a system for the recovery of water from urine. Processes involving the use of external power yield a satisfactory product only after extensive post treatment, usually involving physical chemical methods. This investigation centers on the evaluation and possible development of physical chemical methods for the conversion of urine into water suitable for drinking or other uses in fallout shelters and other isolated sites.

The capacity of the multiple and mixed bed ion exchange for the demineralization of urine; and of activated carbon for the removal of urea, foaming agents, and color were evaluated. Reaction rates and products were determined for the oxidation of urea with calcium hypochlorite and with nitrous acid. The hydrolysis of urea without buffer using the enzyme urease was explored. A strongly acidic sulfonated polystyrene exchange resin was found to be effective for the removal of urea from urine. Experiments on the precipitation of chloride and carbonate, either present in urine or a reaction product, with silver salts were conducted.

A water recovery system synthesized from physical chemical processes for short term missions (210 man-day) is equal or superior to the best available (although no process is yet fully feasible) process developed for water recovery in the space field when compared on a volume requirement basis.

In general, the capacity of physical chemical processes for the removal of a constituent from an aqueous solution is substantially higher than the corresponding capacity for the removal of the same constituent from urine. The control of foaming is a major consideration in the chemical oxidation of urea in urine. For demineralization of urine, multiple bed ion exchange functions at 1/4 the rated capacity; mixed bed, at 3/4 the rated capacity. Activated carbon adsorbs urea to the extent of 4.8%, by weight; and removes one molecule of chloride ion for each molecule of urea adsorbed. Color substances and foaming agents in urine is reduced simultaneously with the removal of urea. The capacity of IR120 exchange resin for the removal of urea from urine is 1/2 the rated capacity. For the oxidation of urea in urine, 140% the stoichiometric quantity of hypochlorite and 150% of nitrous acid is necessary.

Dietary control of the intake of protein by an individual can reduce the amount of urea excreted by a factor of 2 to 7 and should be exploited and practiced, if possible.

Key words: water recover, urine conversion, ion exchange, adsorption,
fallout shelters, oxidation of urea.

INTRODUCTION

In addition to individual family shelters there exists a trend toward moderate and large-size, community fallout shelters suitable for 30 or more persons. In addition to radiation shielding, survival in such shelters would depend upon an adequate air, water and food supply. The standard recommendation for a comfortable water supply is two quarts per day per person. Shelters are normally stocked with a two weeks' food supply, and since an individual can survive two or more weeks without food, a minimum of a four weeks' water supply should be considered as the optimum quantity. The space required for storage, at the recommended rate of consumption of 15 gallons per person per month, would be approximately 100 cubic feet for 50 persons. In shelters, it is generally desirable to minimize the space required for storage.

In any environment, the control of communicable disease is connected intimately with water supply and waste-water disposal problems. If a stored water supply is to be used, continuous surveillance of the quality of the water is necessary. A process which both provides a continuous potable water and simultaneously solves the problem of urine disposal is desirable. In any event, potential public health hazards and nuisances associated with the handling of urine must be controlled.

Most existing methods for the production of drinking water from urine, such as distillation, dialysis, etc., require an external source of energy. A physical chemical process which occupies a minimum amount of space, which has a capacity to meet varying demands, and which does not require an external energy supply is advantageous from the points of view of survival and practicality. Such a system could provide water for drinking or other domestic purposes for an extended period of time.

The development of such a process would involve the removal of objectionable materials from urine in order to produce a high-quality water. The design would include considerations of capacity, geometry, service life, and product quality.

Objective

A series of physical-chemical processes for the conversion of urine into a continuous supply of drinking water was evaluated for the purpose of developing a water recovery system. Such a scheme would have greatest utility in emergency cases where no external source of water or power is available, e.g., fallout shelters and other isolated sites to which a group of people may be confined for a period of time.

Scope of Work

A great deal of effort has been focused on the research, design, and development of systems for the recovery of water from urine for manned space flights. Of the many processes investigated, e.g., electrolysis, cell-fuel cell, freeze crystalization, membrane electrodialysis, vacuum distillation, vacuum pyrolysis, vapor compression, etc., none are presently operational nor practical. The effects of ingestion of recovered water have been studied only for the distillation process with post treatment of vapor or distillate. It is generally concluded that physico-chemical methods of treatment are suitable for missions of short duration only. While it is generally recognized that the quality of water recovered from most processes involving heat is so poor as to require extensive post treatment (usually physico-chemical methods), very little work has been aimed at developing these post-treatment methods as the primary recovery process.

Because of the short mission character of the present problem and the desirability of minimizing the external power requirements of any emergency unit, the present studies are aimed at developing one or a series of physicochemical processes for the recovery of water from urine. Greater emphasize has been placed on investigating processes for the removal of urea as contrasted to investigating processes for the removal of inorganic or ionic constituents. Technology for reducing the ionic concentration of sea water has been developed during World War II in connection with providing emergency desalting kits for pilots.

Schemes for the removal of urea from urine were suggested by available methods for its analytical determination. Ion exchange; enzymatic hydrolysis; precipitation; oxidation of urea with nitrous acid and calcium hypochlorite; and adsorption of urea on activated carbon were investigated. Demineralization of urine, using multiple and mixed bed ion exchange columns operated on an acid-base, silver-base, and silver-chloride cycle, was explored. Treatment of urine with a mixed bed of ion exchange resins plus activated carbon was also evaluated. Urea precipitates considered were urea-nitrate, urea-paraffin, and urea-xanthydrol. Combination of precipitation and oxidation methods are discussed whenever the oxidation products of urea are ionic.

The water quality criteria of potability as promugated by the U.S. Public Health Service reflect a summary of our experience with surface waters and are not applicable to the problem at hand, although widely misused by the uninitiated scientists and engineers who are not aware of the basis for the standards. In this study, the gross constituents of urine after the various treatment processes are indicated but no conclusions with respect to potability are made prematurely.

PERTINENT CONSIDERATIONS

The water balance in man is sensitive to environmental conditions, dietal condition, diet, body weight, and the level of activity. For an adult, under normal circumstances, 1 ml of water is required per Calorie of food intake. Since water is supplied partly through food and partly through the oxidation of the hydrogen of the food, approximately 1 liter of water per day must be drunk to maintain the water balance. The volume of urine under normal conditions for an average-size man is 1.25 l per day. Thus a water recovery system based on the purification of urine must operate on an 80% volumetric efficiency.

The chemical and physical characteristics of urine vary with the diet of the individual and the length of time elapsed between excretion and analysis. For example, the excretion of urea ranges from 4.7 gm/day for persons on a low protein diet to 31.5 gm/day for persons on a high protein diet (1); ammonia may be present in large amounts as a result of the decomposition of urea. Table I. (2) gives a partial listing of the constituents of urine and their respective average daily quantities excreted by normal healthy individuals. Any listing of the constituents is necessarily incomplete because of the presence of many trace compounds and the difficulties associated with microanalysis for these compounds. The two gross constituents are urea and sodium chloride. Other materials which are excreted in amounts greater then one gram per day are creatinine, potassium, phosphates and sulfates. An analysis of excretion products in urine in greater detail may be found elsewhere (3) (4). It is of interest to note that the ionic concentration of urine is approximately 60% of that in sea water; if the urea is chemically converted to ionic compounds, the ionic concentration of urine becomes 3-3.5 times that of sea water.

Table I. Analysis of Normal Human Urine

Constituents	Grams/1250 cc.
urea	30
creatinine	1.15
ammonia	0.7
uric acid	0.7
hippuric acid	0.7
amino acids	0.5
glucose	0.3
aromatic hydroxy acids	0.06
oxalates	0.015
sodium chloride	15.0
phosphates (as P_2O_5)	2.5
inorganic sulfates (as SO_3)	2.0
organic sulfates (as SO_3)	0.3
neutral sulfur (as SO_3)	0.3
potassium (as K_2O)	2.5
calcium (as CaO)	0.2
magnesium (as MgO)	0.2
silicates	0.4
iron	0.005

Williams, R. D., "An Introduction to Biochemistry," D. Van Nostrand Cand Co., N.Y., 1931.

It appears that the amount of urea excreted can be reduced substantially by use of a low protein diet (1), thus facilitating the recovery of water from urine. Urea intake by humans caused diuresis, but no permanently harmful effects (5). A high degree of urea removal from urine is desirable though not critical. The formation of ammonia from the decomposition of urea needs to be prevented due to the high toxicity of ammonia.

The southwestern United States have used water containing 4,000 mg/l of total dissolved solids as drinking water on a continuous basis. A water containing 1,000 mg/l dissolved solids is considered reasonably good. A dissolved solids content of 10,000 mg/l induces some salt toxicity (6). For comparison purposes, an isotonic solution is approximately 9,000 mg/l of NaCl. For emergency conditions, drinking water of 5,000 mg/l dissolved solids is tolerable. The exact tolerable level is immaterial since the efficiency of urine treatment processes to be adopted would be essentially constant for a tolerable dissolved solids content less than 10,000 mg/l. In general a 90% demineralization is required.

The distillation of urine produces highly odoriferous compounds (7). The vapor must be catalytically oxidized at 1200 °F or other extensive post-treatment must be employed to produce an acceptable distillate (8). It is desirable, therefore, to avoid the use of heat in the purification of urine, apart from the limitation of power imposed by an emergency situation.

Summary of Problem Requirements

A process for the recovery of water from urine for use in fallout shelters should operate preferably without external power, have a volumetric recovery efficiency of greater than 80%, provide greater than 90% removal of the gross constituents, and compete with the storage of water. The excretion of urine by normal individuals is 1.25 l/day with a urea content of 24 gm/

a low protein diet) and a mineral content of 0.6 eq/l. Estheti

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national Standards for Drinking Water by WHO and the PHS Drinki

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normal individuals is 1.25 l/day with a urea content of 24 gm/l (4 gm/l for a low protein diet) and a mineral content of 0.6 eq/l. Esthetic considerations of taste, odor, and visual appearance are of importance in determining an acceptable water.

Suspected toxic conversion products must be limited to acceptable concentrations based upon physiological effects, e.g., NO_2^- (10 mg/l). International Standards for Drinking Water by WHO and the PHS Drinking Water Standard may be used as crude guides for general chemical, physical and bacteriological criteria.

ION EXCHANGE

The utilization of ion exchange as a method of treating urine has been explored to a very limited extent. Bonting (9) made use of ion exchange resins in laboratory analysis of urine. He established the total cation content of urine by removing all of the cations with a small ion exchange column and by determining the quantity of hydrogen ions in the effluent. He reported that better than 99 percent removal was achieved from contacting 0.7 meq. of cations with the exchange resin; he did not consider the capacity of the resin. McNeel (10) attempted to develop a method of waste disposal in aircraft by passing urine through a combined anion-cation exchanger and then by permitting the effluent to be picked up by a large wick for evaporation into a warm air stream. It was found that the resins were exhausted after the passage of 400 ml. of urine. A few additional references have been made in the literature to the use of ion exchange as a final purification technique following distillation or freeze-drying.

Multiple Bed Ion Exchange

The ion exchange resins adopted for use in this study were produced by the Rohm and Haas Company. Amberlite IRA 402, a quaternized chloromethylated polystyrene, was chosen as the anion exchanger. It is a strongly basic resin with a moisture content of 40-50% and a suggested capacity of 4.4 meq. per gram (dry basis). Amberlite IRC 50, a poly(methacrylic acid), was chosen as the cation exchanger. It is a weakly acidic resin with a moisture content of 44-55% and a suggested capacity of 8.0-10.0 meq. per gram (dry basis). It was decided that for the initial studies untreated urine should be the influent to the resins.

Cylindrical glass columns, 24 inches in length with an inside diameter of 1 7/8 inches, were used to hold the resins. At the bottom of each column was placed 3/4 inch of glass wool followed by six or seven glass marbles and by another 3/4 inch layer of glass wool. The resin was then added and occupied approximately 12 1/2 inches of length of the column, 330 grams (dry basis); another 3/4 inch of glass wool was placed on top of the resin to prevent splattering of the influent and to diffuse the influent over the entire surface of the resin. The influent was delivered at 10 ml. per minute through a 600 ml. seperatory funnel attached at the top of the column.

Two columns were operated in series with untreated urine being passed through the column containing IRA 402 (anion exchanger) and with the effluent from the anion exchanger being passed through IRC 50 (cation exchanger). This order was adopted to provide an influent to the IRC 50 with a high pH. The urine was collected from six male adults over a period of several days and was stored at a temperature of 1-4 °C. During the storage periods there were no signs of degradation; the color, odor, and pH remained unchanged. The effluents were generally collected in 250 ml. batches and were kept refrigerated until being subjected to analysis.

Analyses were carried out to determine the average characteristics of the influent to the anion exchanger and of the influent to the cation exchanger. Similar tests were applied to a series of effluent samples from each column. Hydrogen ion concentrations were determined with a Beckman pH meter. Absorptivity measurements were made with a Klett-Summerson photoelectric colorimeter, using a number 42 filter (400-465 mμ). The zero point of the instrument was set with distilled water, and the absorptivity measurements were converted to color units by comparison with standard solutions containing potassium chloroplatinate and cobaltous chloride (11). Total solids were determined by evaporation of the samples to dryness at 103-105 °C. Sulfate ion was analyzed by precipitation with barium chloride, followed by ignition of the filter residue at 800 °C. Chloride was determined volumetrically using silver nitrate and potassium dichromate, and sodium and potassium ion concentrations were measured with a flame photometer. Calcium was analyzed by a modification of the standard permanganate test and by the EDTA titration method (11). An analysis of untreated urine is presented in Table II. This represents the average composition of the influent to the anion exchange column.

Experimental Results

The first series of observations was made by passing four liters of untreated urine through the anion exchanger. The first 2000 ml. of effluent were collected in 250 ml. samples, while the last 2000 ml., after the resin break point had been reached, were collected in 500 ml. samples. The prescribed set of analyses was made on each sample and the results were tabulated on the basis of cumulative volume of effluent (throughout volume). The analysis for each 250 ml. sample was assumed to apply to 125 ml. of throughput volume and for each 500 ml. sample, to 250 ml. of volume. Fig. 1 presents the relation of the pH of the effluent to the throughput volume. The first point indicated applies to the second sample collected; the first sample did not provide a proper measure of the effectiveness of the resin, since a large portion of the first 250 ml. consisted of the water which was used in preparing the resin for operation. It may be observed that a sharp break in the effectiveness of the resin occurs at 1600 ml. of throughput and that the resin is virtually exhausted when 2000 ml. of effluent have been collected.

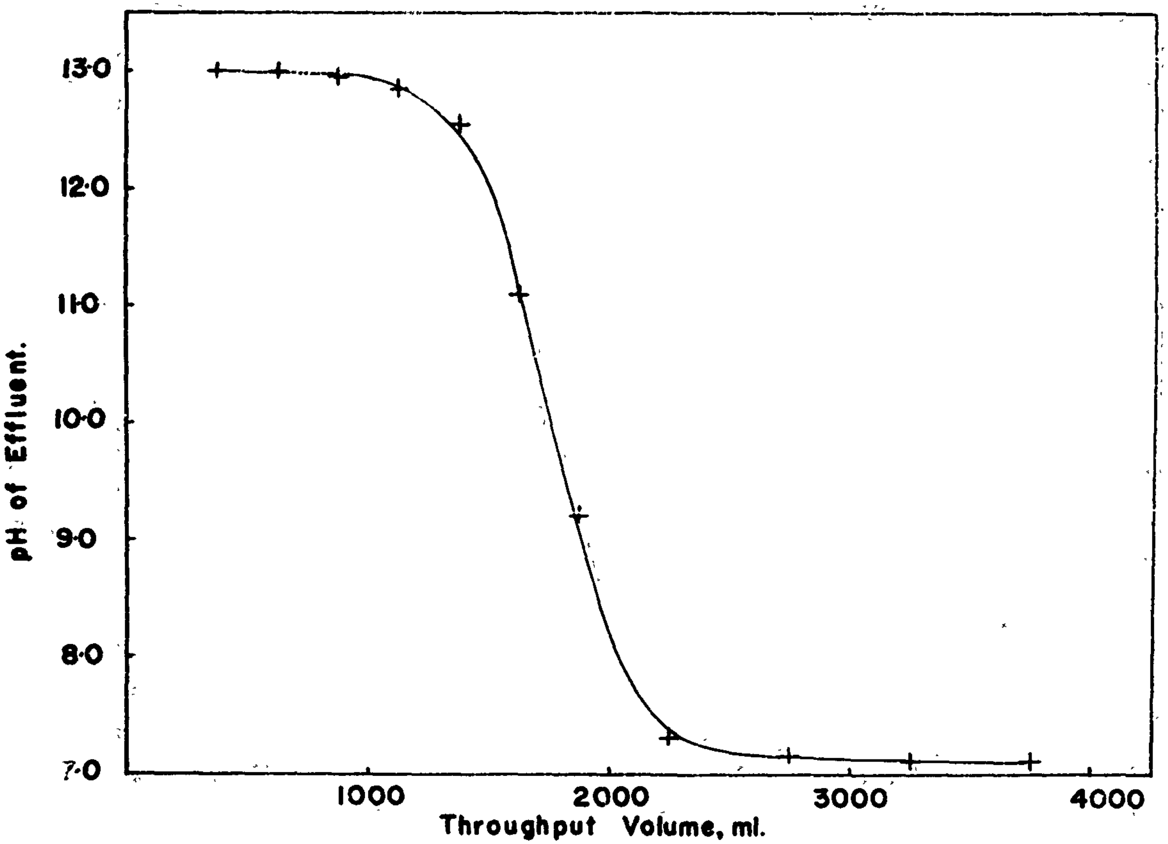

Fig. 1 Variation in pH of Effluent from Anion Exchanger.

Fig. 2 indicates the relation between the ratio of the effluent chloride concentration to that in the influent and the throughput volume. A similar relation for sulfate is presented as Fig. 3. The resin appears to be exhausted with respect to chloride removal sooner than with respect to sulfate removal and sulfate is still being removed until 4000 ml. of effluent have been collected. The resin's greater capacity for the divalent ion is to be expected. The results of the tests for total solids show a fraction of 0.53 of the solids in the influent remaining for 500 ml., 0.79 for 1000 ml., and 0.97 for 1500 ml. The value of this determination is lessened by the presence of large amounts of urea.

Two sets of color tests were run on the effluent samples; one set was made one day after the column operation, and the other, three days after the operation. The results are presented in Fig. 4. In the first day tests a definite turbidity began to appear in the samples which corresponded to 1500 ml. or more of throughput volume. This in part accounts for the relative maximum in the first day curve. The third day tests were made to see if the turbidity was reduced by sedimentation to any extent; some reduction had taken place, but a definite cloudiness appeared in the last three samples. Filtration of these samples caused no significant change in the absorptivity. The turbidity effects can be explained in part by the sloughing-off of calcium phosphate by the resin. It is also possible that bacterial action could have occurred; however, the samples were kept refrigerated except during analysis.

The second series of observations was made by passing the combined effluent from the anion exchanger through the column containing IRC 50. It was decided that more representative results could be obtained by using only the initial effluent from the anion exchanger as feed for the cation exchanger. The first 1600 ml. of throughput volume was of rather uniform concentration

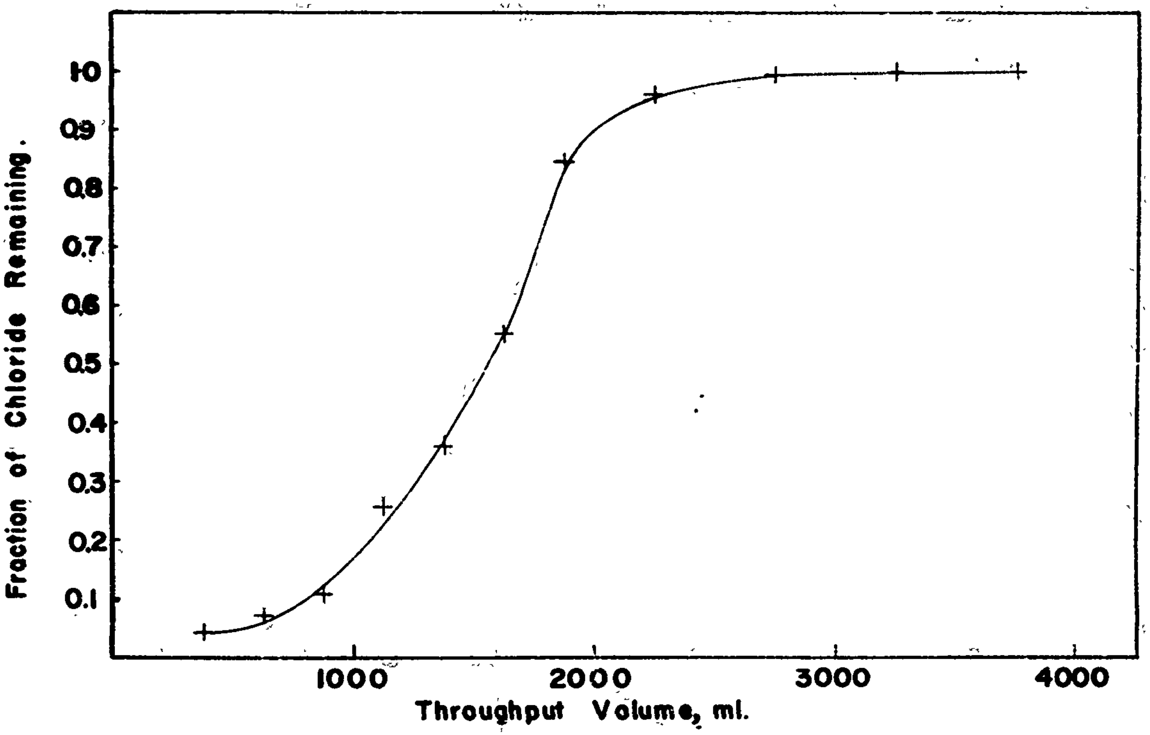

Fig. 5 Variation in Chloride Concentration of Effluent from Anion Exchanger.

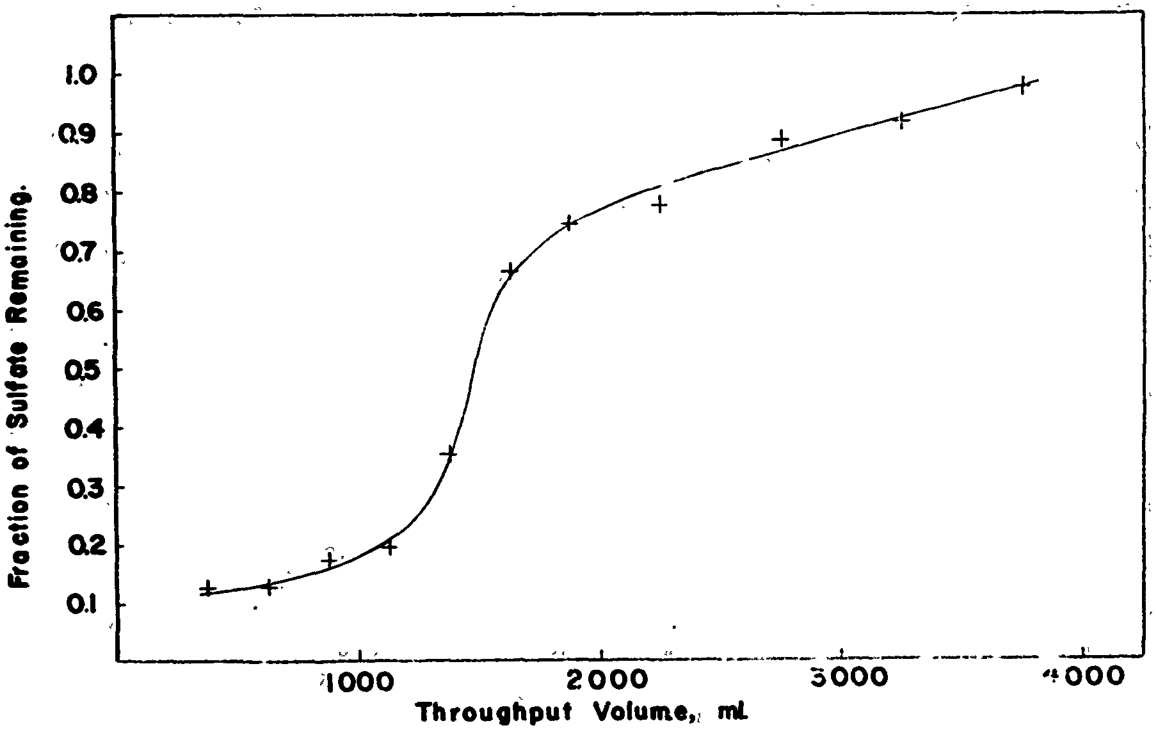

Fig. [illegible] Variation in Sulfate Concentration of Effluent from Anion Exchanger.

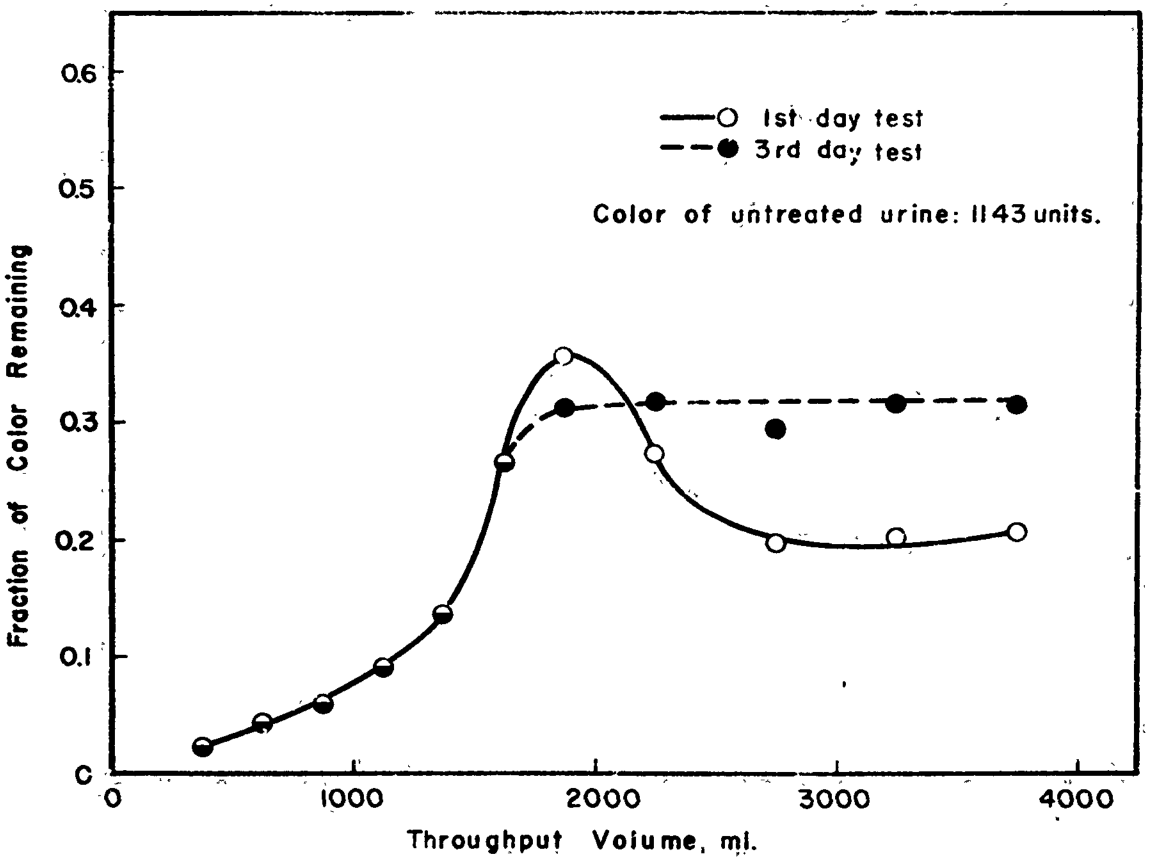

Fig. [illegible] Variation in Color of Effluent fr[illegible] Exp. [illegible].

and represented the effluent from an effectively operating anion column. As a result, three anion exchange columns were set up and 1600 ml. of untreated urine were passed through each column. The results of the analysis are presented in Table III. The total absence of calcium ion should be noted. It is likely that the calcium was precipitated out in the anion exchanger as calcium phosphate; this was enhanced by the elevated pH at which the anion exchanger operated. Although no quantitative analysis was made for magnesium, it seems probably that this cation was also precipitated out as magnesium hydroxide; this was qualitatively determined from the permanganate calcium analyses.

About 4750 ml. of the combined anion exchanger effluent were passed through the cation exchanger. Table IV indicates the variation of the pH of the effluent with throughput volume. It may be observed that the column was still operable after 4100 ml. of effluent had been collected. The break point occurs at approximately 4500 ml. of throughput. The results of the sodium and potassium analyses are also presented in Table IV. It can again be seen that the column was operating effectively up to the 4500 ml. point. The remaining fraction of total solids in the effluent during the period before exhaustion was on the average approximately 0.35 that of the influent. The color of the effluent was reduced to about 0.5 of that of the influent until a throughput volume of 3000 ml. was reached. It then rose sharply due to turbidity.

From the results which have been presented it may be observed that the anion exchanger removed approximately 260 meq. of chloride and 80 meq. of sulfate before the resin was exhausted. This corresponds to 1.03 meq. per gram of dry resin. Approximately 1500 ml. of untreated urine were processed

Table II. Analysis of Untreated Urine

Test	Results
pH	6.6
color	1143 units
chloride	6.8 gm./l.
sulfate	1.5 gm./l.
calcium	0.25 gm./l.
sodium	3.7 gm./l.
potassium	3.3 gm./l.
total solids	37.6 gm./l.

Table III. Analysis of Influent to Cation Exchanger

Test	Results
pH	12.6
color	90.0 units
chloride	1.0 gm./l.
sulfate	0.5 gm./l.
calcium	0.0 gm./l.
sodium	3.7 gm./l.
potassium	3.3 gm./l.
total solids	28.4 gm./l.

Table IV. Analysis for pH, Sodium, and Potassium of Effluent from Cation Exchanger

Throughput Volume (ml.)	pH	Sodium (gm./l.)	Potassium (gm./l.)
125	3.4	1.0	0.95
625	3.4	0.8	0.7
2125	4.0	0.55	0.8
4125	5.0	0.55	0.8
4625	10.4	0.75	1.8

before the resin approached exhaustion, although sulfate was still being removed until the 2500 ml. point. This corresponds to four ml. of effluent per cm^3 of resin. In addition, significant quantities of calcium and magnesium were removed, apparently by precipitation; this may have influenced the rapid exhaustion of the anion exchanger by forming a film to block available exchange sites. The cation exchanger removed approximately 500 meq. of sodium and 250 meq. of potassium before the resin was exhausted. This corresponds to 2.27 meq. per gram of dry resin. About 4500 ml. of effluent were collected before the resin approached exhaustion; this corresponds to 11 ml. of effluent per cm^3 of resin. The combination of both columns produced an effluent with a total solids content 0.27 of the value for the influent. The total solids removal is greater than would be expected from the sulfate, chloride, sodium, and potassium analyses. This may be attributed to exchange of other ions, some urea removal, and the filtering action of the exchange beds. The color of the effluent was 40 units compared to 1143 units for the influent. Urea removal was negligible.

Mixed Bed Ion Exchange

Mixed bed ion exchange refers to the practice of using a mixture of cation and anion exchange resins in a single bed. Such an arrangement allows the salt splitting reactions in the exchanger to proceed toward completion more rapidly than in multiple bed ion exchange.

A mixed bed ion exchanger employing cation and anion exchange resins and activated carbon was evaluated for the treatment of urine. In general, the amounts of ion exchange resins and activated carbon used in a column were estimated from the individual capacities previously determined.

Information on the combinations summarized in Table V was obtained. Amberlite IR 120, a strongly acidic sulfonated polystyrene; IRA 410, a strongly basic quarternary ammonium polystyrene, aminated with dimethylethanol amine, were employed as exchange resins. Coconut activated carbon, 6-14 and 50-200 mesh, was used for color removal. Breakthrough curves for urea, sodium, and chloride are shown in Fig. 5 UCR* ratios are shown in Table V.

The average concentrations of the gross constituents of urine used as feed were urea (20.4 gm./l.); K^+, Na^+ (7.0 gm./l.) and chloride (9.3 gm./l.). An overall UCR of 2.4, 3.5, and 3.0 were obtained based on the breakthrough points for urea, chloride, and sodium, respectively. The mixed bed ion exchange capacity compared with the sum of capacities of individual components is approximately twofold. The use of silver base cation exchange resin with an hydroxide base anion resin resulting in additional removal of chloride by precipitation did not improve the UCR since urea concentration in the effluent was the limiting factor. It appears that the use of mixed bed ion exchange, employing silver base cation, hydrogen base cation, and hydroxide base anion resins is best suited for the treatment of urine first freed of urea.

In terms of demineralization, the silver base cation resin gave a UCR of greater than 7. However the presence of Ag_2O in the effluent makes the exclusive use of silver base cation resin impractical. Resin capacity for removal of urea from urine is approximately 1/2 the capacity for urea removal from aqueous solution; for demineralization, 1/4 the rated capacity for multiple bed operation and 3/4 the rated capacity for mixed bed operation.

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*Volumetric ratio of urine treated to chemicals required for treatment.

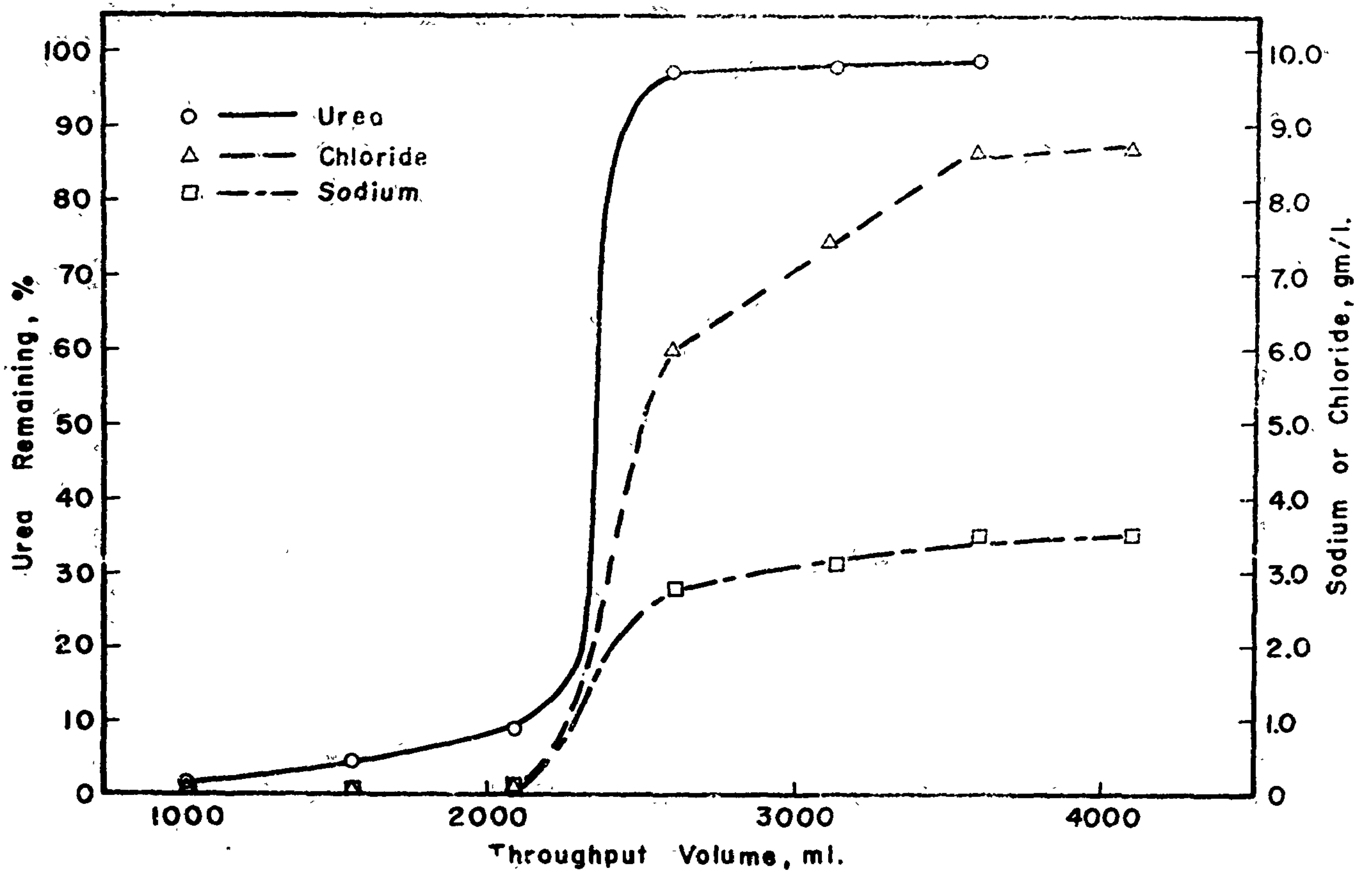


Fig. 5 Breakthrough Curves for Mixed Bed Ion Exchange.

Table V. Urine Purification with Mixed Bed Ion Exchange

Item	401	402	403	404	405		403		406	409
Cation Exchange Resin										
Type IR120	(H^+)	(Ag^+)	(Ag^+)	(Ag^+)	(Ag^+)	(H^+)	(Ag^+)	(H^+)	(Ag^+)	(H^+)
Amount, gm	280	500	250	330	100	100	270	100	300	330
Anion Exchange Resin										
Type IRA410	(OH^-)	(OH^-)	(OH^-)	-	(OH^-)	-	(OH^-)	-	(Cl^-)	-
Amount, gm	300	20	150	-	100	-	100		100	-
Activated Carbon										
Type, Mesh	(6-14)	(6-14)	(6-14)	-	(6-14)	(50-200)	(6-14)		(6-14)	-
Amount, gm	250	200	250	-	75	200	240		250	-
Flow Rate, ml/min-cm^2	3.6	3.6	3.6	4.0	3.0		3.0		3.0	4.0
Column Volume, Liters	1.6	1.0	1.0	0.33	1.0		1.0		1.0	0.33
Urea in Urine, gm/l	18.9	19.4	19.5	20.0	21.0		22.0		22.0	21.5*
UCR Ratio	1.5	2.6	3.7	2.2	1.5		2.5		2.5	4.7

*aqueous solution

Urea Removal by Ion Exchange

The capacity of IR 120 (H^+) ion exchange resin for the removal of urea from aqueous solution was found to be approximately 2.5 times the capacity of 6-14 mesh coconut activated carbon. For urea removal from urine, the capacity ratio was approximately 2. The capacity of the exchange resin for removing urea from urine is approximately one-half its capacity for removing urea from an aqueous solution. Fig. 6 shows a comparison of the breakthrough curves.

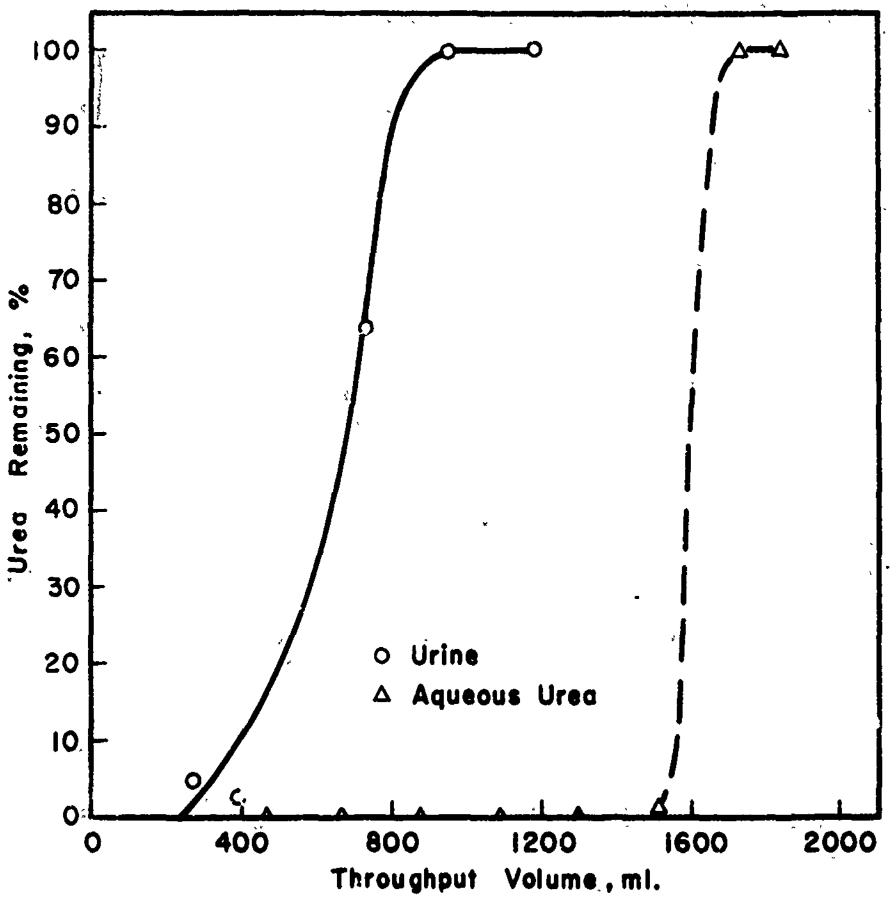


Fig. 6 Urea Removal with Ion Exchange Resins.

ADSORPTION OF UREA AND COLOR WITH ACTIVATED CARBON

The adsorption of the weakly ionized compound urea by the nonpolar adsorbent activated carbon can be described by the Freundlich adsorption isotherm equation,

$$x/m = K\, c^{1/p} \qquad (1)$$

where

x = amount of urea adsorbed,

m = weight of activated carbon,

c = equilibrium concentration of urea in solution

x/m = concentration of urea in the adsorbed state, and

K, p = constants.

In liquid phase adsorption, the transfer of adsorbate molecules from the bulk solution to the carbon surface is followed by migration of the adsorbate from the surface to the adsorption sites within the carbon particles. The latter is generally the rate controlling step and the rate of adsorption will increase with an increase in the ease of accessibility of sites (larger surface area, smaller particle size). Conditions contributing to the success of urea adsorption from urine by carbon are (1) urea is a relatively small molecule (high diffusivity), (2) the concentration of urea in urine is large in comparison with other compounds which may compete for the available adsorption sites, and (3) water is not strongly adsorbed by carbon.

Adsorption columns of two different particle size, coconut, activated carbon (6-14 and 50-200 mesh) were employed to study the adsorption of urea from urine. The service time and critical depth of column; the shape of the adsorption wavefront and the adsorption wavelength; and the capacity of the activated carbon were determined.

Service Time

Column service time is defined as the time necessary for the effluent concentration to reach some arbitrarily chosen value (quality of effluent). One of the most successful theory for the description of column operation is the Bohart-Adams surface reaction rate theory (12). Briefly, the change in concentration of urea as a function of time and position is due to diffusion and adsorption

$$\frac{\partial c}{\partial t} + v\frac{\partial c}{\partial z} = D\frac{\partial^2 c}{\partial z^2} + R \qquad (2)$$

where

c = urea concentration,

t = time,

v = velocity of flow through column interstices,

z = column ordinate in the direction of flow,

D = proportinality constant, and

R = rate of urea adsorption by column.

Neglecting molecular diffusion and writing Eq. (2) in terms of the porosity (α) and local rate of urea removal ($\partial n/\partial t$),

$$\frac{\partial c}{\partial t} + v\frac{\partial c}{\partial z} = -\frac{1}{\alpha}\frac{\partial n}{\partial t} \qquad (3)$$

Relating the rate of irreversible adsorption to the column capacity,

$$\frac{1}{\alpha}\frac{\partial n}{\partial t} = K_1\, c(N_0 - n) \qquad (4)$$

where

N_0 = column capacity, gm per gross volume,

$(N_o - n)$ = column capacity at any time, and

K_1 = a constant,

i.e., the rate of removal is a first order reaction. Eqs. (2) and (4) result in the Bohart-Adams equation

$$\ln(c_o/c - 1) = \ln(e^{K_1 N_o z/v} - 1) - K_1 c_o t \qquad (5)$$

where

c_o = initial urea concentration.

The service time (t_s) is given approximately by:

$$t_s = \frac{N_o}{c_o v} z - \frac{v}{K_1 N_o} \ln(c_o/c_e - 1) \qquad (6)$$

where

c_e = arbitrarily tolerated urea concentration in the effluent.

Critical Column Depth

The critical column depth (z_c) is the value of z just sufficient to obtain an effluent concentration of urea $\leq c_e$ at $t = 0$.

$$z_c = \frac{v}{K_1 N_o} \ln(c_o/c_e - 1) \qquad (7)$$

Capacity of Activated Carbon

The column capacity is determined by the slope of t_s vs z; and the rate constant K_1, by the intercept. The maximum capacity is dependent upon:

(1) the shape of the adsorption isotherm, p,

(2) the critical dolumn depth, z_c,

(3) the flow rate, v,

(4) the particle size of the adsorbent, K_1, and

(5) the arbitrarily tolerated urea concentration in the effluent, c_e.

Methods

Analytical procedures for urea; color; pH; and total and fixed solids have been described previously. The activated carbon column preparation was as follows. The carbon was first soaked in hot distilled water to purge adsorbed gases. A one inch plug of glass wool followed by a one inch layer of glass beads served as support for the carbon. Care was taken to maintain a one inch water seal above the carbon surface during packing of the columns.

An 8 ft. head, gravity system was available for the regulation of urine flow rate. Qualatative test for chloride in the effluent, employing acidified silver nitrate, was used to detect the initial emergence of treated urine, giving the chloride wavefront speed.

Experimental

The adsorption isotherm for aqueous urea solution at 26 °C shown in Fig. 7 indicates that the adsorptive capacity of coconut, 6-14 mesh activated carbon increases nearly linearly with urea concentration. For urea concentration equal to 24 gm./1., x/m = 0.074, i.e., adsorption capacity is 7% by weight. Fig. 8 shows color and urea removal by 6-14 mesh coconut activated carbon column with urine as feed. The small volume of urea free effluent indicates that the adsorption wavelength is greater than the column depth used, >23". The column continues to function effectively for color removal pass the urea breakthrough point.

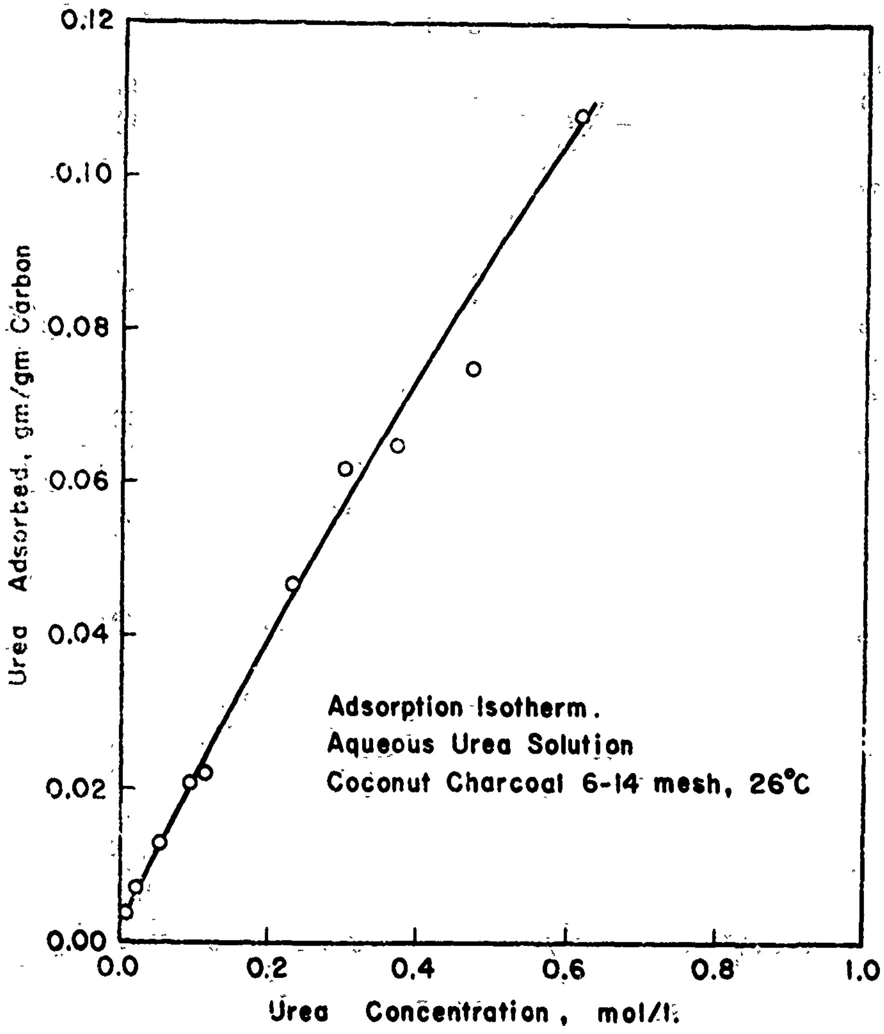


Fig. 7 Adsorption Isotherm for Urea-Activated Carbon System.

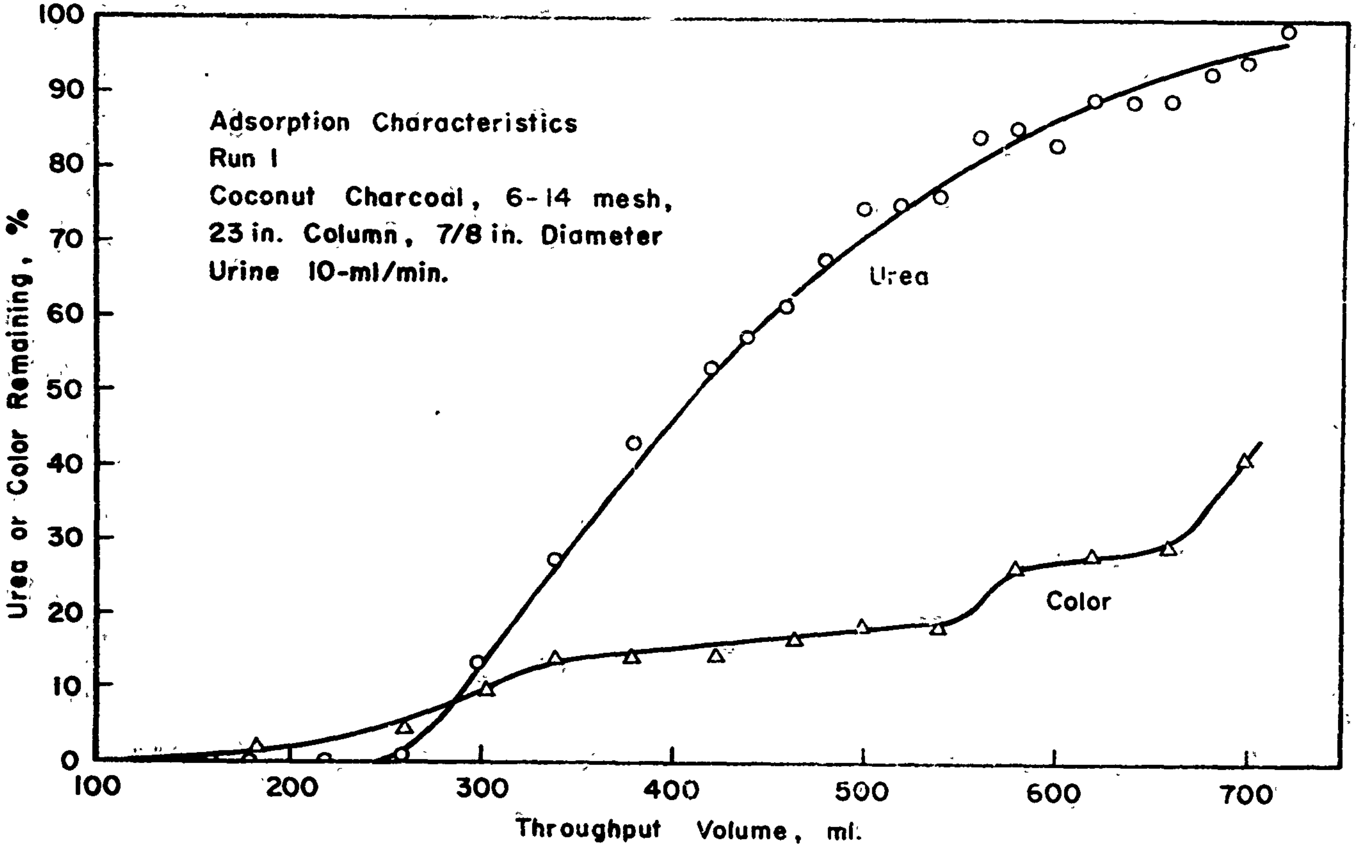


Fig. 8 Urea and Color Adsorption by Coconut Charcoal.

Three columns of 45" carbon depth per column (470 gm. each) were operated in series and the effluents from each of the columns were analysed routinely for urea and pH; and, less frequently, for color and chloride. The shapes of the wavefronts for each of the columns are shown in Fig. 9. The capacity for column 1, found by graphical integration of the wavefront, was 22.5 gm. urea/470 gm. carbon or 4.8%. This compared with a maximum adsorptive capacity of 7% for aqueous urea. The percentage of fixed and total solids remaining was 42% and 92%, respectively. Fixed solids were slightly reduced, indicating some ionic adsorption (hydrolytic effect). Total solids were reduced substantially, reflecting urea removal. The variation in pH also was largely due to urea removal and may be used as an indicator of the urea breakthrough point. See Fig. 10. The breakthrough point for color follows the breakthrough point for urea, although the entire color wavefront was not determined. Urea breakthrough points for columns 1, 2 and 3 were respectively 1040, 2320, and 4630 ml. The corresponding wavelengths based on 5% of the original urea concentration in the respective effluents and a constant wavefront speed of 0.5 in./min. (urea detection in effluent) were 19, 13, and 20 in. Service time for a single column was approximately (45-19)/0.5 = 52 min. Adsorption capacity of the activated carbon for urea from urine was computed from Eq. (6) and experimental values of t_s. Values of t_s vs. z are shown in Table VI. N_c was found to be 0.038 gm. urea per cm^3 gross volume of activated carbon; K_1 computed from Eq. (5) and the average experimental value of wavelength (19 in.) was found to be 0.034 cm^3 gross volume per gm. urea adsorped per sec.

Adsorption of urea from urine with 50-200 mesh coconut activated carbon is shown in Fig. 11. The wavefront is essentially square, i.e., wavelength small and the adsorption rate constant K_1 large. The breakthrough point is

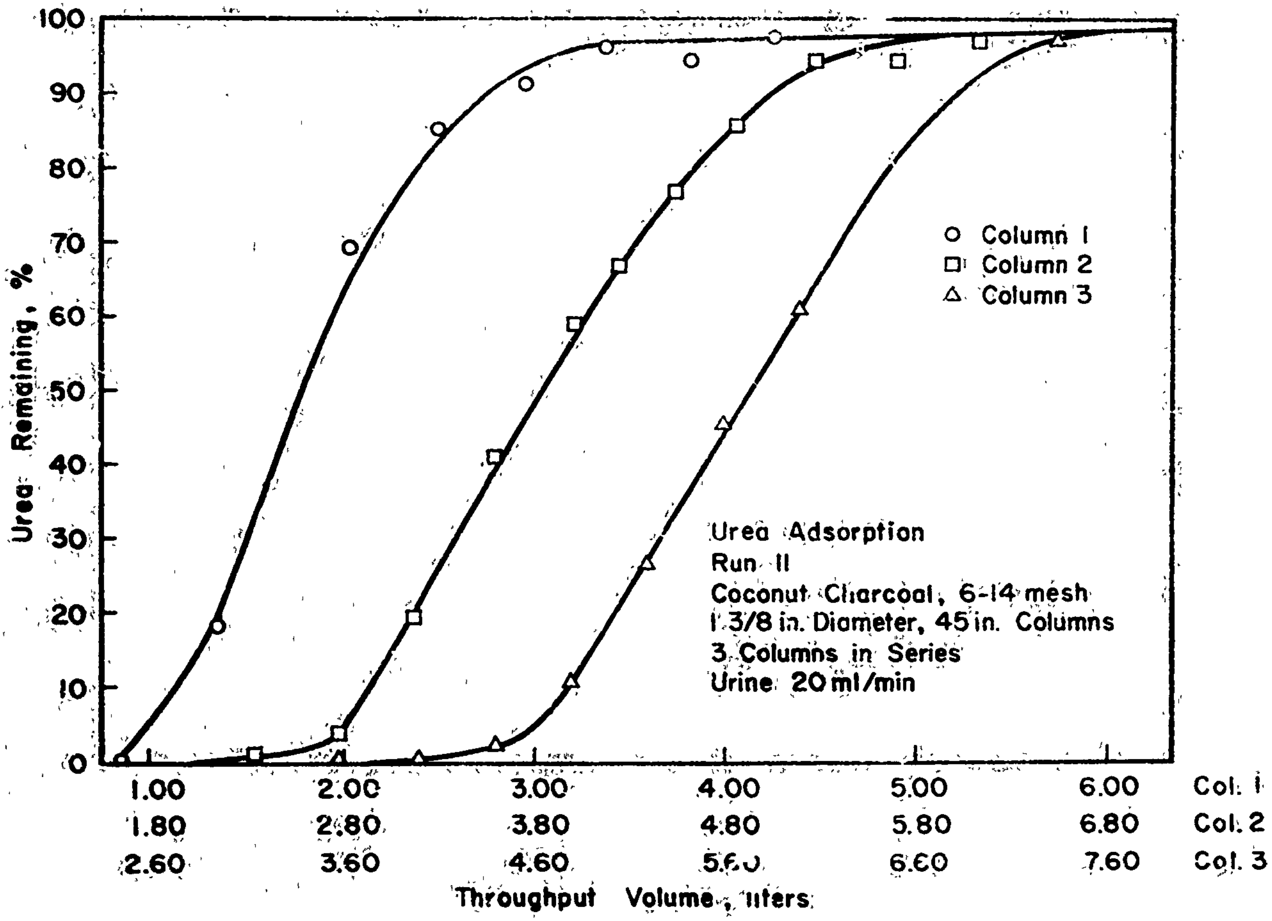


Fig. 9 Urea Adsorption by Coconut Charcoal.

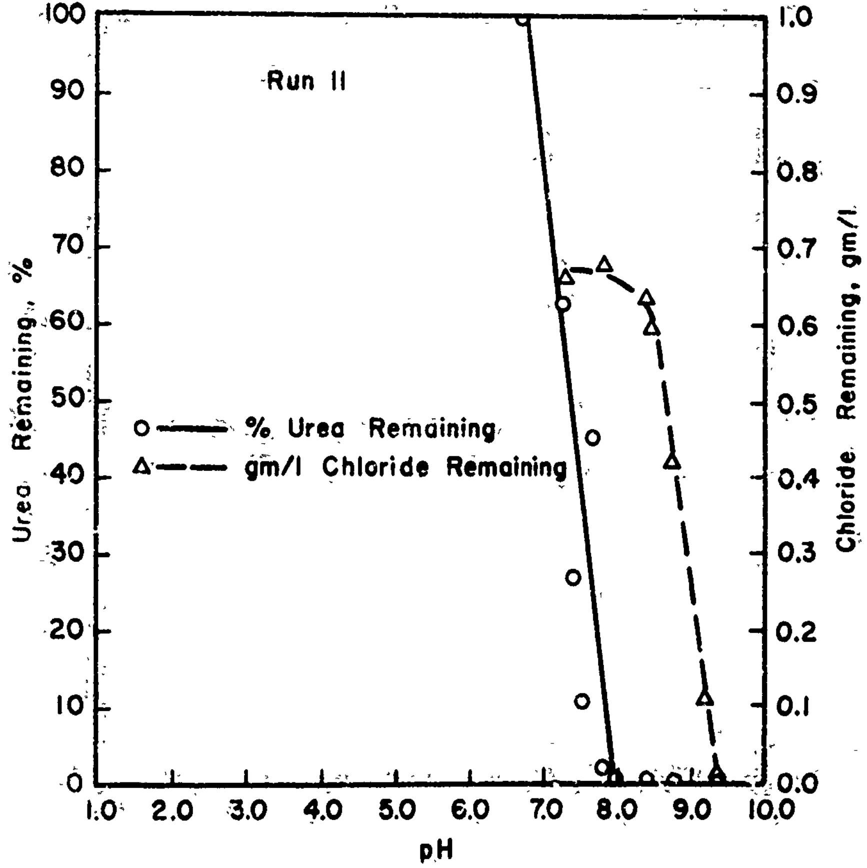


Fig. 10 Urea and Chloride Remaining vs. pH.

Table VI

Activated Carbon Column Performance Coconut, 6-14 mesh

Column Length, z, cm	Urea Concentration c_o, gm/cm^3	Volume Urea Treated Q, cm^3	Interstice Velocity, v, cm/sec	Service Time, t_s, sec
57	0.0193	293	0.021	1760
114	0.0227	1040	0.050	3120
228	0.0227	2800	0.050	8450
342	0.0227	4630	0.050	13,900

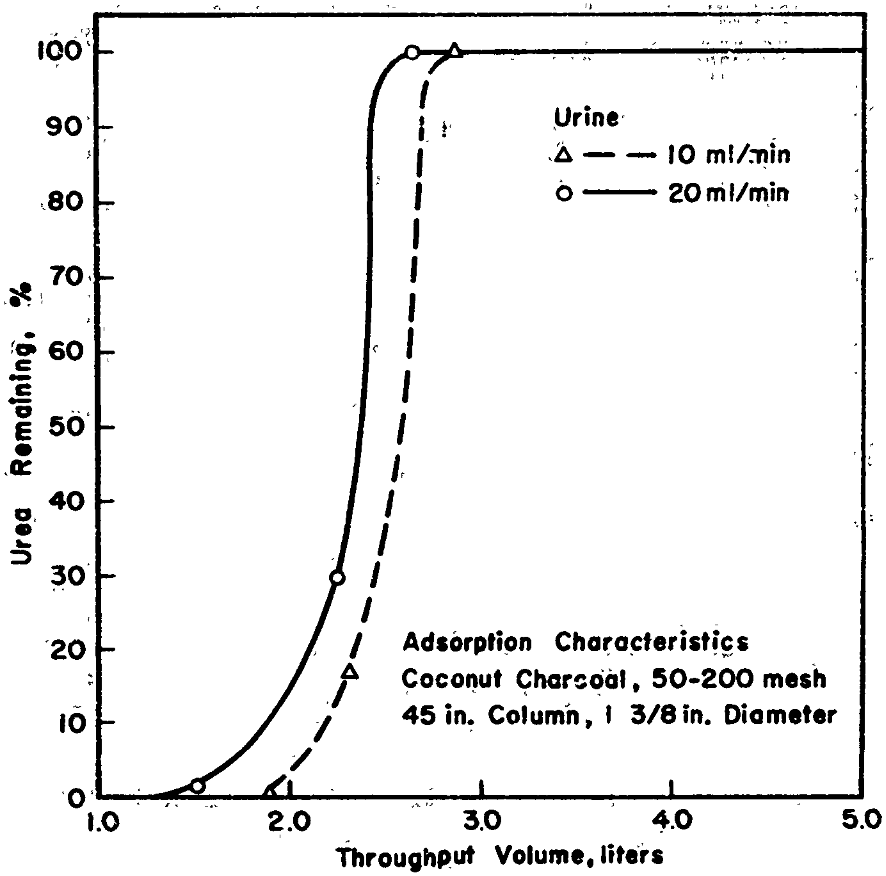


Fig. 11 Urea Adsorption by Coconut Charcoal.

defined more sharply for 50-200 mesh carbon than for 6-14 mesh carbon. For the fine size activated carbon, increasing the contact time from 45 to 90 minutes only increased the urea adsorption from 14.5 to 18.2 gm. ($c_e \leq 5\% c_o$). A 16% increase in the adsorption capacity is accounted for due to the difference in the urea concentration of the feeds. Doubling the contact time, therefore, increased N_o by 10% (N_o = 0.04 gm./cm^3). The ratio of adsorptive capacity of 50-200 mesh to 6-14 mesh activated carbon was found to be 2 (contact time 90 min.).

For urea removal, a UCR of 2.4 is possible for 50-200 mesh activated carbon and, UCR of 1.2, for 6-14 mesh. Increasing contact time beyond service time improves the urea adsorptive capacity of activated carbon but slightly. The Bohart-Adams equations are sufficient for estimating column performance characteristics. Adsorption capacity for urea from urine is approximately 5/7 the maximum capacity obtained with aqueous urea solution. Actual adsorption capacities were 0.038 and 0.045 gm. urea from urine per gross cm^3 6-14 and 50-200 mesh activated carbon, respectively. The reaction rate constant is sufficiently large and not a major column design parameter.

OXIDATION OF UREA

Two methods for the chemical oxidation of urea in urine were evaluated. The first method involves the use of calcium hypochlorite, a commonly available compound. The second method employs nitrous acid as the oxidizing agent. This method suffers from the disadvantage that nitrous acid must be made in situ but has the advantage that the products of oxidation are entirely gaseous.

Oxidation of Urea with Calcium Hypochlorite

Aqueous urea solution (24 gm urea/l) and urine (28 gm urea/l) were treated with HTH calcium hypochlorite (65% available chlorine). The available chlorine content of the HTH was determined by titration with 0.1N sodium thiosulfate and potassium dichromate; urea concentration, by the McLean ureometer.

The oxidation of urea may be represented by the overall chemical equation

$$2CO(NH_2)_2 + 3Ca(OCl)_2 = 2CO_2 + 2N_2 + 4H_2O + 3Ca^{++} + 6Cl^- \quad (8).$$

For an aqueous urea solution (24 gm urea per l), complete oxidation of urea was achieved with a 125% of the stoichiometric quantity of calcium hypochlorite. The oxidation reaction was accompanied by precipitation of calcium carbonate. Approximately 24% of the calcium content of calcium hypochlorite added was thus removed in the oxidation step. The approximately linear variation of the percentage of urea oxidized with increasing amount of hypochlorite is shown in Fig. 12. For the oxidation of urea in urine, 140%

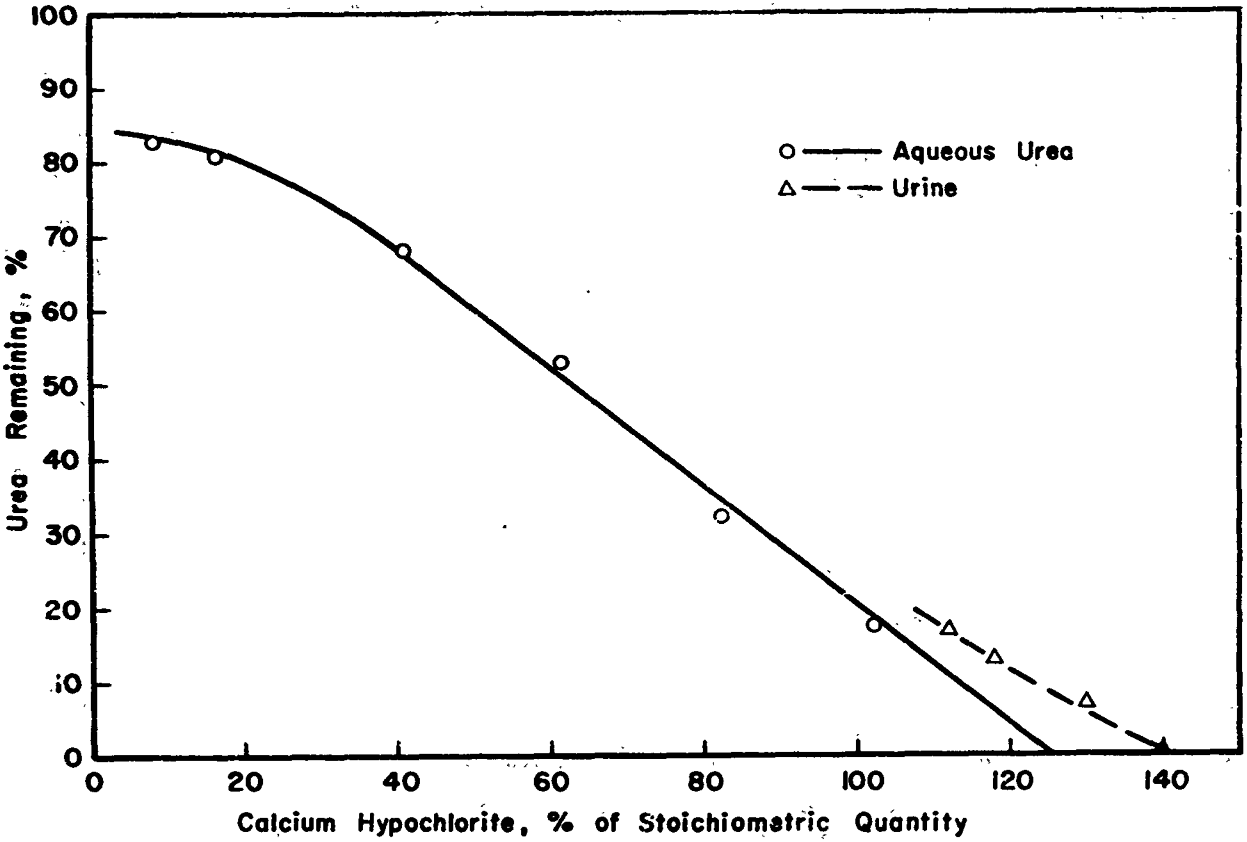


Fig. 12 Oxidation of Aqueous Solution of Urea and of Urine by Calcium Hypochlorite.

of the stoichiometric amount of hypochlorite was needed for complete oxidation.

A stable, rather voluminous foam was formed when a hypochlorite was added to urine. This was not observed with aqueous urea. Three methods were considered to overcome this difficulty: 1. the use of a screen as a mechanical foam breaker, 2. the addition of a small amount of defoaming agent to the urine (such as a silicone derivative) which could later be absorbed from the urine, 3. the use of a preliminary absorption step to remove the surface-active agents present in urine. The third method seemed most promising, particularly if some urea removal could be accomplished. Mechanical and chemical foam breakers were unsuccessful. The filtration of urine through activated carbon (25 ml per gm carbon) reduced the foaming considerably.

Precipitation of calcium and chloride ions in solution resulting from oxidation of urea would be necessary if ion exchange were to follow. Introduction of silver and carbonate ions into a solution containing calcium and chloride ions seemed likely to precipitate silver chloride and calcium carbonate since the solubility products of these compounds are extremely low. Four precipitation methods were evaluated: 1. use of a saturated solution of silver carbonate in ammonium hydroxide, 2. use of dry silver carbonate, 3. use of silver carbonate followed by silver oxide, and 4. use of dry silver oxide. Complete removal of both calcium and chloride ions was effected by methods 1 and 2, using approximately the stoichiometric quantity of silver carbonate (based on chloride content). The calcium to chloride content was 0.7 on an equivalent basis. Analysis showed that addition of silver carbonate beyond the requirement for complete precipitation of calcium continued to precipitate chloride, but introduced undesirable carbonate ions into solution. It was therefore decided to attempt a two stage precipitation (method 3) using silver carbonate for precipitation of all the calcium and part of the chloride, followed by silver oxide for removal of the remaining chloride. The use of ammonium hydroxide as a solvent for the silver carbonate did not seem to aid the precipitation reaction appreciably; dry silver salts were used in all further experiments. Complete removal of both calcium and chloride ions was effected by the two stage precipitation. Silver carbonate additions were in stoichiometric quantities based on the calcium content and silver oxide, in 130% of the stoichiometric quantity based on the remaining chloride content. The solution after complete precipitation of calcium and chloride was highly alkaline. This could presumably be attributed to hydrolysis of silver oxide.

In alkaline solution dissolved carbon dioxide exists as the carbonate ion and in the presence of calcium ions is likely to precipitate as calcium carbonate. Since silver oxide has both the property of removing chloride ions in solution as well as increasing the alkalinity of the solution, oxidation of urea with calcium hypochlorite in the presence of silver oxide (method 4) seemed likely to precipitate both the reaction products, calcium and chloride. An aqueous solution of urea was contacted with 125% of the stoichiometric quantity of calcium hypochlorite and 130% of the stoichiometric quantity of silver oxide based on chloride content. Complete precipitation of both calcium and chloride ions was effected. However, only 90% of urea removal was effected, indicating some interference.

Two methods for the oxidation of urea with calcium hypochlorite and for the precipitation of the reaction products, calcium and chloride ions, seem feasible:

Oxidation with hypochlorite followed by precipitation first with silver carbonate, then with silver oxide.(method 3),

Simultaneous oxidation and precipitation, using calcium hypochlorite and silver oxide. (method 4).

Table VII compares the properties of the solutions after treatment by the above methods and presents a comparison of the chemical requirements. It can be seen that the economics of method 4 seem more favorable than that of method 3, since the price of silver oxide is approximately half that of silver carbonate.

Table VII. Analysis of Solutions Before and After Precipitation Treatment

Property	Initial Solution	Final Solution Method 3	Final Solution Method 4
pH	7.0*	12.2	12.4
Ca^{+2}, gm/l	33.2	---	---
Chloride, gm/l	66.6	---	---
Alkalinity as $CaCO_3$			
OH^-, gm/l	---*	23.20	18.50
CO_3^{-2}, gm/l	---*	3.14	9.50
HCO_3^-, gm/l	---*	---	---
Urea, gm/l	24.0*	---	2.50

*before oxidation

Chemical Requirements

Chemical	Consumption gm/l urea solution Method 3	Consumption gm/l urea solution Method 4
Calcium hypochlorite	150.9	169.0
Silver carbonate	180.0	---
Silver oxide	82.5	305.8

Oxidation of Urea by Nitrous Acid

The oxidation of urea in aqueous solution and in urine was investigated to determine the extent and rate of reaction and reaction products. The overall oxidation is represented by

$$CO(NH_2)_2 + 2HNO_2 = CO_2 + 2N_2 + 2H_2O \qquad (9)$$

The conversion of urea into only gaseous compounds is ideal from the standpoint of water recovery. In principle, urea is removed without increasing the ionic concentration significantly, e.g., the use of silver nitrite and hydrochloric acid. Nitrous acid is known only in solution and was generated in situ by the addition of an acid followed by a gradual addition of a nitrite.

Experimentally, the extent of oxidation of aqueous urea or urine with nitrous acid was determined by measuring the urea concentration prior and subsequent to oxidation. The rate of reaction was measured my measuring the rate of gas production. Gas collection was by means of a spirometer sealed with a saturated salt solution whose pH was low. The products of the oxidation and the dominant reactions were surmised from analyses made on the liquid and gaseous phase.

A number of available analytical techniques and laboratory procedures required modification and/or testing to validate the method for application under the particular conditions imposed by either the type or concentration of compounds present. The possible interference of ammonia on the urea determination with the Mclean ureometer was found to be negligible. The acidity of the sample did not interfere with the determination if a 1 ml sample was used. The nitrogen content in the liquid, as determined by the alkaline reduction method (11), cannot distinguish between ammonia and nitrogen at a higher oxidation state. It was necessary to analyse for ammonia separately by distillation and prior to the nitrogen analysis by the alkaline reduction method. The presence of urea does not give a positive nitrogen test by the reduction method. The phenoldisulfonic acid test(11), specific for nitrate, was found to be unsuitable due to interference from the nitrite in the sample.

Analysis of carbon dioxide in the gaseous products was initially made with an Orsat apparatus. Subsequent analysis with the barium hydroxide method (13) showed that there were at least two acidic gases formed by the oxidation of urea with nirtous acid. A mass spectrum of the gaseous products obtained from a mass spectrometer showed the two major acidic gases to be carbon dioxide and nitric oxide. The measurement of the rate of gas production presented no difficulties.

The experimental procedures adopted were as follows. The concentration of urea in the mother liquid and in the liquid after oxidation were determined with the Mclean ureometer, employing 1 ml samples. Ammonia in the liquid after oxidation was found by the distillation method; the nitrogen remaining, by the alkaline reduction method. The volume of gas produced was measured at one-minute intervals, up to 15 minutes when the reaction was essentially completed. A grab sample (usually 30 ml) was used for the analysis of both carbon dioxide and nitric oxide by a modification of the barium hydroxide method. The total acidity was found by titration with hydrochloric acid; carbon dioxide, from the weight of barium carbonate formed; and nitric oxide, from the difference between total acidity and the acidity due to carbon dioxide. A mass spectrum was also obtained on separate grab samples corresponding to the same time interval.

Experimentally, 0.84 moles HNO_2 oxidized 0.46 moles urea, giving a yield or efficiency of 30%. Results for several schemes of HNO_2 formation are summarized in Table VIII. Low yields are associated with phosphoric acid, an incompletely dissociated acid; high yields are associated with sulfuric acid, a strongly dissociated acid. Yields obtained with aqueous solutions and with urine are similar, indicating little interference, despite the complex composition of urine. Foaming was encountered in the oxidation of urine. This can be minimized by slowly adding nitrite in solution form.

The volume of gas produced versus time is shown in Fig. 13. The rate o. reaction is small after 10-15 minutes. The volume of gas produced at the end of 10, 12, 15 and 60 minutes are 1.19, 1.21, 1.22, and 1.26 l respectively.

The acidity of the gas was found to be considerably higher than can be accounted by carbon dioxide alone. A comparison of typical values for the oxidation of 25 mmol urea with a stoichiometric quantity of nitrous acid is shown in Table IX. The acid gases were absorbed in water or barium hydroxide and the determination of nitrogen in the absorbent was positive, indicating the presence of some form of oxide of nitrogen. The gaseous products, upon exposure to air, assumed a reddish-brown appearance. This lead to the hypothesis that nitric oxide was present and upon oxidation gave the characteristic color of nitrogen dioxide.

Confirmation that nitric oxide was a major gaseous product from the oxidation of urea with nitrous acid was obtained from two additional sources. Table X shows the relative values of the significant peaks obtained from several mass spectra. No peaks were found between mass numbers 47-108; the peak associated with a mass number of 30 corresponds to the excess acidity noted above, adding assurance that the excess acidity was due to nitric

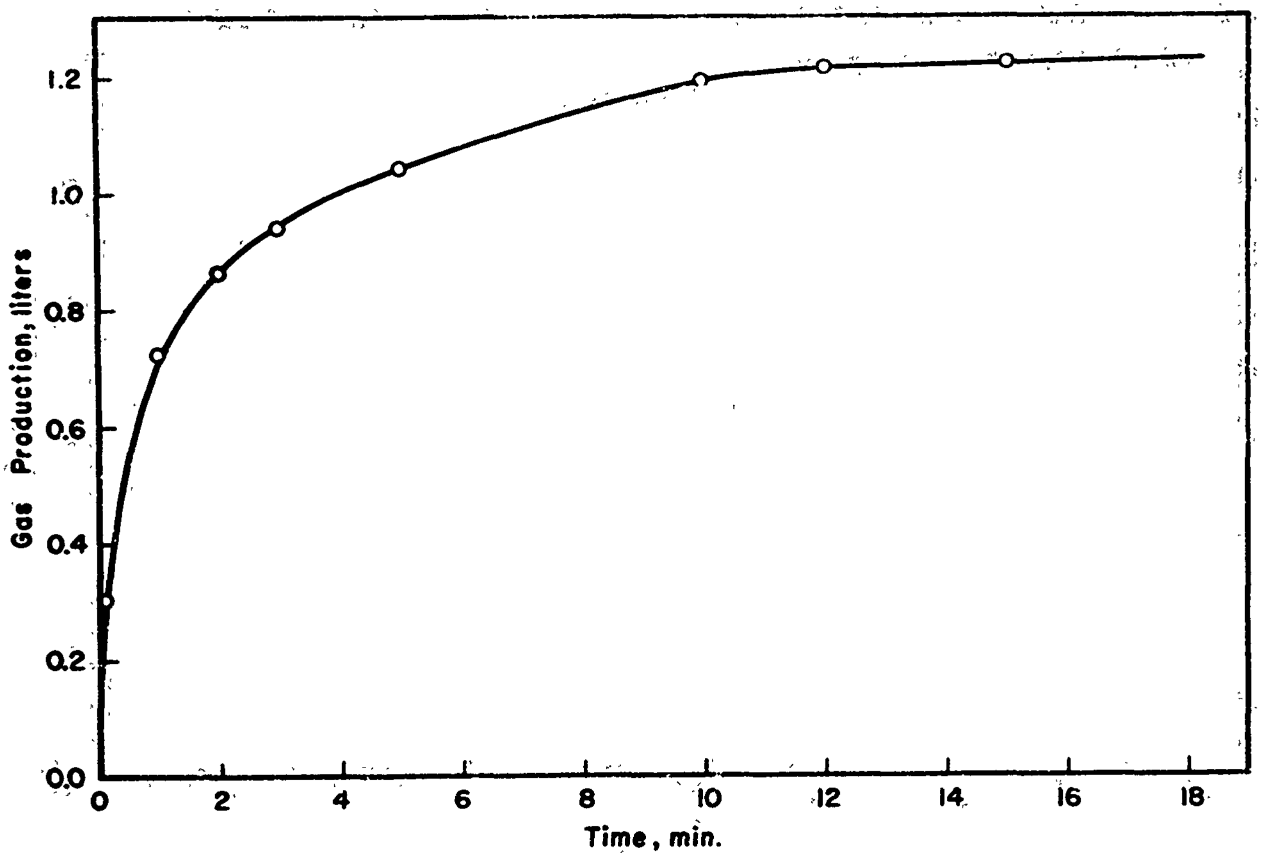


Fig. 13 Gas Production as a function of Time for the Oxidation of Urea with Nitrous Acid.

Table VIII. Oxidation of Urea by Nitrous Acid

	Run	Urea, mol/1	Nitrite, mol/1	Acid, eq/1	Exesss Nitrite	Effluent Nitrite*, gm/1	Effluent Urea Oxidized, %
Aqueous Urea Solution	1	0.46	0.96	1.08	no	n.a.	>86
	2		0.84	0.99	no		78
	3		0.49	0.84	no		60
	4		1.66	0.84	yes		84
	5		0.84	0.84	no		84
	6		0.97	0.95	yes		85
	7		1.73	1.14	yes		84
	8		1.62	1.43	yes		85
	9		0.84	0.91	no	9.1	51
	10		0.84	0.91	no	10.3	51
	11		1.25	1.14	yes	-	64
	12		2.51	2.29	yes	-	85
	13		1.74	1.57	yes	28.2	81
	14		0.84	0.98	no	1.4	81
	15		0.84	1.47	no	5.2	78
	16		0.84	1.47	no	6.1	80
	17		0.84	1.47	no	6.2	79
	18	0.46	0.84	1.47	no	5.6	80
Urine	19	0.38	0.80	0.85	no	n.a.	77
	20	0.41	1.07	0.84	yes		82
	21	0.46	1.07	0.86	yes		84
	22	0.34	0.81	0.86	no	12.0	74

Note: n.a. = not available

*See discussion on page

Table III. Acidity of Gaseous Products (Based on oxidation of 25 mmol urea in aqueous solution)

	Total Acidity, meq.	Carbon Dioxide, meq.	Other Acid Gases, meq.
	46.1	24.8	21.3
	47.8	23.2	24.6
	41.6	27.7	13.9
	43.6	28.1	15.5
	44.0	30.1	13.9
	32.0	22.6	9.4
	36.0	23.2	12.8
Ave.	41.6	25.7	15.9

Table X. Mass Spectrum of Gaseous Products

Mass No. Item	Gas Volume, %		
	N_2, 28, 29	NO, 30	CO_2, 44, 45, 46
A	68	12	20
B	78	1.5	20.5
C	65	12	23
D	63	15	22
E	60	12	28
Ave.*	64	13	23

Chemical Tests Item	Gas Volume, %		Total Volume, l
	NO	CO_2	
A	14.4	22.7	-
B	1.3	20.2	1.69
C	11.5	23.3	1.39
D	15.6	23.0	1.42
E	10.2	24.1	-
Ave.*	13	23	1.4

*excludes B

oxide. The sensitivity of the alkaline reduction method of nitrogen determination to oxides of nitrogen was evaluated. Nitric oxide, nitrous oxide, and nitrogen dioxide were dissolved in water and the nitrogen content of the adsorbent determined. The results added further evidence that the excess acidity was nitric oxide. The oxides of nitrogen used had a minimum purity of 99%. While nitric oxide and nitrogen dioxide are soluble to some extent and nitrous oxide is very soluble in water, nitrous oxide gave a negative test with the alkaline reduction method. The use of the Saltzman method for analysis of nitrogen dioxide (14), a specific test for nitrite, ruled out its presence in the gaseous products; the mass spectrum confirmed this. A positive test for nitrogen in the adsorbent indicated was nitric oxide is present but does not rule out the possibility of nitrous oxide since both compounds have a mass number of 44. The excess acidity together with the mass spectrum indicate that nitrous oxide was present in small quantities compared with nitric oxide and carbon dioxide. See Table X.

The sensitivity of the reduction nitrogen test to the three oxides of nitrogen are summarized in Table XI. For reasonable accuracy, a water to gas volumetric ratio of three should be used for the absorption step. A minimum volumetric ratio of 10 was adopted for expediency.

Free ammonia and total nitrogen content of the aqueous urea solution after oxidation are given in Table XII. The presence of free ammonia indicates that one of the major reactions involved in the oxidation of urea is hydrolytic. The quantity of nitrogen present as ammonia accounts for roughly one-half the total nitrogen. The remainder of the nitrogen is nitrite-nitrate.

Table XI. Sensitivity of the Alkaline Reduction Nitrogen Test to Oxides of Nitrogen

Gas	Volume Ratio, Water/Gas	Detection, %
N_2O	0.2	1
	1.0	0
	5.0	0
NO	0.2	7
	0.4	16
	0.6	17
	1.0	41
	2.2	79
	3.0	86
	4.0	100
NO_2	0.1	35
	0.2	45
	0.9	64
	1.8	99
	3.5	100

Table XII. Ammonia and Total Nitrogen Tests on Oxidized Urea Solution. (Based on oxidation of 25 mmol aqueous urea solution)

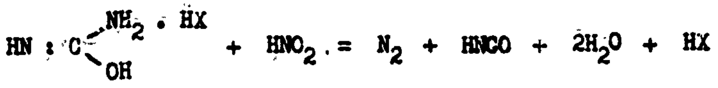
	Ammonia, mg N	Total Nitrogen, mg N	Ammonia, %
	107	212	50.5
	108	240	45.0
	121	234	51.7
	126	280	45.0
	122	253	48.2
	101	255	39.6
	122	225	54.1
Ave.	115	24.3	47

A synopsis of the major reactions involved in the oxidation of urea, synthesized from the experimental results and known equilibria, is as follows. The reaction is essentially complete in 10-15 min. The gaseous products identified are nitric oxide, nitrogen, carbon dioxide, and water. The presence of a relatively large concentration of nitrogen compounds remaining in the treated urea solution is due partly to acid hydrolysis of urea and partly to the equilibrium between water and nitric and nitrous acids,

$$3HNO_2 = H^+ + NO_3^- + 2NO + H_2O \qquad (10)$$

The equilibirum constant for the reaction is $K = 30$; the equilibrium is the principal source of nitric oxide in the gaseous products and of nitrogen in the oxidized urea solution. Because of the equilibrium, specific nitrite and nitrate tests cannot distinguish between nitrite and nitrate. The formation of a relatively stable foam when urine is oxidized may be minimized by pretreating urine with activated carbon or by controlling the rate of nitrous acid formation.

The major reactions involved in the oxidation of urea with nitrous acid are



$$HN:C{<}^{NH_2\,\cdot\,HX}_{OH} + HNO_2 = N_2 + HNCO + 2H_2O + HX \qquad (11)$$

$$HNCO + H_2O = NH_3 + CO_2 \qquad (12)$$

$$HNCO + HNO_2 = CO_2 + N_2 + H_2O \qquad (13)$$

$$3HNO_2 = H^+ + NO_3^- + 2NO + H_2O \qquad (10)$$

The volume of gas resulting from oxidation of 25 mmol urea with a stoichiometric amount of nitrous acid was found to be 1.4 l or 57 mmol; the composition of the gas on a dry basis was: carbon dioxide, 23%; nitric oxide, 13%; and nitrogen, 64%. The quantity of ammonia and nitrite-nitrate present in solution was 8.5 mmol each. The yield of the oxidation was 80% with respect to urea. The small percentage of carbon dioxide formed indicated that the reaction represented by Eq. (12) kept some of the carbon dioxide in solution.

MISCELLANEOUS METHODS

Urea forms a precipitate with paraffins whose chain length is greater than six carbon atoms. The paraffins are insoluble in water, hence a common solvent for urea and dodecane or some other paraffin is necessary. The use of methyl butanone serves as the common solvent and urea-paraffin crystals form in the solvent. The partition coefficient for urea in a water-methyl butanone system favors the precipitate formation only when the concentration of urea in the water phase is near saturation. This scheme has a potential UCR of 50.

Dixanthydryl-urea compound is insoluble in the presence of a little acetic acid and is readily formed. The high molecular weight and the combining ratio of two molecules of xanthydrol to one molecule of urea gives a potential UCR for the urea removal step of four; an overall estimated UCR of 2.5.

The hydrolysis of urea by the enzyme urease is well documented (15)(16). The hydrolysis product, ammonium carbonate, presents difficulties for the subsequent treatment method whether it be electrodialysis; distillation or an allied method; or a physico-chemical method. The urea in urine may be completely hydrolysed in a buffered solution (pH 6.5-7.0) in two hours. Our results, using unbuffered urine, indicate 25 hours are necessary.

The removal of ammonium carbonate from solution is difficult. The work of Brown, et.al.(17), showed that only 10% of the amonia was lost in 2-5 hrs when a hydrolysed sample of urine was subjected to an average absolute vacuum of 10-25 mm Hg. The precipitation of ammonium magnesium phosphate or ammonium calcium phosphate is possible by the addition of calcium hydroxide to a hydrolysed sample of urine buffered with phosphoric acid. Our results indicate that 60% of the water in urine is associated with the precipitate as water of hydration. See Table XIII.

Table XIII. Precipitation of Ammonium Carbonate

NH_4CO_3, meq	Ammonia Reacted, %	Water Recovered, %
200	61	56
100	56	62
100	66	72

System Synthesis

System synthesis, the selection and combination of processes for the recovery of water from urine, may be made on the basis of information developed in this study, knowledge gained from studies related to the manned space vehicles (NASA), and the experiences of World War II. Systems which are feasible at present do not have necessarily an overwhelming advantage over the storage of water.

The capacities of the several physico-chemical methods for the purification of urine may be summarized as follows:

1. Mixed bed ion exchange is superior to multiple bed ion exchange. Demineralization capacity for mixed bed ion exchange is approximately 3/4 the rated capacity; for multiple bed ion exchange, 1/4 the rated capacity.
2. The ion exchange resin IR 120 can remove urea from urine; capacity is approximately 1/2 the rated capacity in meq/cm^3 resin.
3. Activated coconut charcoal was effective for the removal of color and urea from urine. The capacity of charcoal is 1/2 that of the IR 120 resin. The main advantage of charcoal is its ability to remove color and frothing agents from the urine. Some chloride is removed due to a hydrolytic reaction.
4. Urea may be oxidized chemically by calcium hypochlorite. Approximately 140% the stoichiometric quantity is needed. The ionic concentration of the urine is increased by the impurities present in the hypochlorite ($CaCl_2$) and by the oxidation products ($CaCl_2$) and reduced through the precipitation of calcium sulfate.

5. Urea oxidation by nitrous acid would require a 50% excess over the stoichiometric requirement. The ionic concentration of the urine is increased due to the nitrite-nitrate equilibrium.
6. The hydrolysis of urea by the enzyme urease is rapid when urine is buffered with respect to pH by the use of phosphoric acid. The product of hydrolysis, ammonium carbonate, remains in solution.
7. Ammonium ion may be precipitated from solution as ammonium calcium phosphate. The compound is highly hydrated and retains up to 50% of the water treated.

For the purpose of comparing the various systems synthesized on some standard basis, the composition of urine may be classified into two major categories: urea (0.4 mol/l); anions and cations (0.3 eq/l each). Guidelines set forth by NASA may be used to assess penalties for power requirement of the system:

> "Electrical power used by the system shall be charged to the weight of the system at a rate of 0.3 lb per watt used."

For the process considered to be the best suited for manned space flight, the vacuum distillation method, post-treatment with 160 gm activated carbon and pre-treatment with 3 ml 98% sulfuric acid were required per man-day of urine (18). There is some doubt as to the potability of the water produced by this process, even with pre- and post-treatment, because of the reported 30-60 ppm of free ammonia in the recovered water.

The emergency kits used for demineralization of sea water for flyers indicate that the capacity of ion exchange resins for demineralization is approximately 0.75 eq per 100 gm resin. The corresponding capacity for treating urine must be reduced in accordance with item (1) above.

A comparison of the systems available for water recover from urine is given in Table XIV; newer processes in the investigative stages are also shown. Power penalty was estimated at 0.4 ft^3, the volume of fuel oil necessary to evaporate water at 100% efficiency. This is a fairly representative figure. For example, the smaller amount of heat required for evaporation at lower temperatures is compensated by the increased energy needed for the compressor in the case of vapor compression.

Some possible systems employing physico-chemical methods are:

1. Mixed bed ion exchange-the use of IR 410 and IR 120 resins for demineralization, IR 120 resin for urea removal, followed by activated carbon for color and odor reduction. The required activated carbon may be divided to give pre- and post-treatment. The pre-treatment enables the ion exchange resins to function more effectively by removing non-polar and weakly ionized organic compounds and suspended solids.
2. Chemical oxidation of urea with calcium hypochlorite followed by precipitation of calcium and chloride; and by ion exchange demineralization. The packaging of the hypochlorite and resins can minimize the bulk of materials required. Color is removed with the precipitation step.
3. The use of zeolites for demineralization followed by activated carbon and IR 120 resin for the removal of urea.

The volume of urine treated to volume of chemical required (URC) ratio of 3 to 4 can be improved by limiting the amount of protein in the individual diet. The excretion of urea can be reduced by a factor of 2-7 (1)(19) with a corresponding increase in the UCh for the physico-chemical methods to a maximum value of 10 but the distillation and associated methods do not benefit from a lower urea content in the urine. Terminal disinfection for the above methods by chemical means should be included.

Table XIV. Representative Figures of Current Water Recovery Techniques

Capacity, 30 lb./day; 14 day mission

(420 lb. or 6.73 ft.^{3})

Process	Volume Ratio[1]		
	Basic[2]	Power Penalty[3]	Pre- and Post-Treatment Included
Freeze Distillation	x	x	x
Vacuum Distillation	x	x	x
Vacuum Pyrolysis	2	1.7	1.4
Vapor Compression	3.5	2.8	2.0
Membrane Electrodialysis*	13*	7.5*	3.7*
Phyico-Chemical Methods	3-4	3-4	3

Comparison of Relatively New Water Recovery Techniques

Capacity, 30 lb./day; 14 day mission

(420 lb. or 6.73 ft.^{3} water)

Process	Basic[2]	Power Penalty[3]	Pre- and Post-Treatment Included
Zone Refining	x	x	x
Electrolysis Cell-Fuel Cell	x	x	x
Spray Condenser	3.5	2.8	2.0
Membrane Permeation	9	?	?
Ultrafiltration	7	7	7
Thermoelectricity	7	?	?

Notes:

1. x denotes volume requirement greater than that required for the storage of water,
2. Stored water/apparatus,
3. Same as note (2) with power penalty, and

* Urea removal not included.

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Mr. Galler and Mr. Lagvankar are both post-master students and have earned credits toward the Ph.D. while employed part time by the project.

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Manuscripts in Progress

1. Performance Characteristics of Activated Carbon Columns for the Treatment of Urine.

2. Determination of Nitrate in Wastes by the Nitron Method.

3. The Oxidation of Urea by Nitrous Acid.

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