

# Ersatz Formulas for Lunar Outpost Wastewater and Brine

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## ABSTRACT

Early development of wastewater and brine processing equipment must rely upon ersatz formulations because authentic urine and hygiene water are variable in composition, difficult to acquire in quantity, and have limited storage life.

Previous wastewater ersatz formulations (e.g. Verostko et al, 2004) were designed for chemical fidelity, to match the elemental ratios and VOC profile of defined blends of wastewater components. This paper presents an alternative spreadsheet approach to brine and wastewater ersatz formulation by combining "building block" recipes in user-selected ratios and accounting for compositional shifts upon evaporation.

## INTRODUCTION

Several methods for brine dewatering are currently under study as alternatives to the AES wick evaporation method initially proposed in the 60's and tested extensively with biologically treated wastewater brines in 2000-2002 (1). Development of brine dewatering equipment is fraught with uncertainty because the wastewater characteristics for Lunar Outpost have yet to be officially baselined with respect to the identity and quantity of surfactants in hygiene water and perhaps laundry water, the pretreatment chemicals to be added to the urine stream, and the volume fractions of urine, hygiene water, laundry water and humidity condensate to be expected in the mix. Until wastewater composition is standardized, brine composition must remain uncertain. Available ersatz formulations developed by Verostko and coworkers (2) and refined by Carrier and coworkers (3) represent specific blends of wastewater

streams. However these, along with the wastewater generation rates for various missions published in the BVAD (4, 5) represent the best available information to date and furnish a suitable starting point for brine ersatz construction.

Brine composition is also affected by partitioning of volatiles in wastewater during evaporation. A 10-fold concentrate of a waste stream may contain all or none of a given volatile component depending on its relative volatility and on processing conditions including temperature and pH. Simply removing water from wastewater ersatzes will generate brine ersatzes artificially enriched in volatile components.

In this paper, the ersatzes developed by prior workers (2, 3) have been recalculated to update the composition of source wastewaters and to facilitate the assembly of brines reflecting single wastewater components, component mixes in variable ratios, and the effect of processing on volatiles.

## BACKGROUND AND ISSUES

**PROS AND CONS OF THE ERSATZ APPROACH.** Ersatzes are well suited for early development of processing strategies for wastewater and brine. Ersatzes can be made up in the laboratory as needed, without requiring the investigator to solicit donations of urine or to construct facilities for hygiene water collection. Ersatz use minimizes exposure of workers to pathogens from donors of urine and graywater, and avoids the issue of bacterial and enzymatic changes such as urea breakdown to ammonia.

Ersatz formulations are uniform in composition, unlike urine in which the total solids concentration, ionic composition, and organic/inorganic pool concentration ratios vary among individuals and fluctuate from day to day depending on diet, water intake, and medications. For example, urine of newborn infants varies in specific gravity from 1.002 to 1.040 (6). Use of pooled urine samples reduces variability, but adds the issue of urine storage. Hygiene water is also variable in composition.

The consistent composition of ersatzes makes them well suited for early equipment development and testing, when variability in process inputs must be controlled to isolate the effects of equipment design and settings on performance.

Ersatzes made of soluble chemicals lack the water-insoluble components typically present in true wastewaters such as skin oils and shed skin cells from hygiene water, toothpaste grit from dental hygiene water, and proteins and menses in urine streams. Ersatzes which match the salt concentration in wastewaters cannot exactly match solubility characteristics of those salts in real wastewaters, due to the natural crystallization inhibitors in urine.

Water and brine processing equipment must gracefully cope with compositional variability, odors, reactive components and insolubles in genuine wastewater streams. For this reason ersatzes cannot replace genuine wastewater in every testing situation. However, as Putnam (7) pointed out:

“For engineering analysis purposes in water reclamation technologies, an abbreviated list of compounds is in most cases more than adequate to characterize human urine. This is not to suggest that there is any substitute for using real urine in the development and testing of water recovery subsystems: rather, that it is convenient, and sufficiently accurate for most analyses, to use a simplified version of the real thing.”

**HISTORY OF ERSATZ DEVELOPMENT.** The first NASA urine ersatzes (8), reported in 1995, were developed to support assessment and flight testing of the Vapor Compression Distillation assembly and the solids retention filter on its recycle tank. Ersatzes were formulated from a mixture of inorganic salts plus soluble urine organics (not including urea, to avoid the possibility of ammonia release) and small amounts of sparingly-soluble organics, e.g. androstenone. After concentration in a rotary evaporator, the ersatzes matched urine in several aspects but failed to precipitate as much solid material as genuine urine, with or without pretreatment. Hence reconstituted pretreated concentrated urine was used as the official ersatz for VCD testing. The urine

pretreatments were specified as 5 g oxone and 2.3 g concentrated sulfuric acid per liter of urine and 316.7 g water per kg urine (equivalent to 323 mL water per L urine at a urine density of 1.02); no potassium benzoate was included.

Campbell and coworkers (1) formulated an ersatz for Early Planetary base humidity condensate which they used in the integrated AWRS tests in 2001-2002. Their formula was based on data from Mir and from Shuttle flights.

In 2004, Verostko, Carrier and Finger (2) provided standard preparation methods for ersatzes of several wastewater streams: Transit and Early Planetary Base (EPB) wastewater streams and partially-reprocessed EPB waste streams such as Biological Water Processor (BWP) effluent, RO permeate of BWP effluent (nominal and worst case), and AES condensate (nominal and worst case). These ersatzes were designed to match the pH, conductivity, TOC, TIC, and chloride content of actual wastewater components in fixed blend ratios and were intended for testing primary wastewater processing and the polishing of treated wastewaters such as RO permeate and AES condensate. The ersatz formulations make up into full strength blended wastewater “working solutions”.

The recipes in Verostko (2) et al have been repeatedly revised and updated. An official revision was released by Carrier and coworkers in 2006 (3). The most significant modification was a change in the insoluble organics concentrate used in ersatzes for BWP effluent, RO permeate and AES condensates. No change was made to any components of transit or EPB wastewater.

Though the 2004 and 2006 ersatz documents provide essential guidance, the ersatz formulae therein are not well suited for work on brine dewatering. They represent “working solution” wastewaters at the solids level initially entering the water reprocessing system, not brines from which both water and solutes have been removed. The 2004 and 2006 formulae also presuppose given ratios of wastewater components and admit no flexibility in the mix of wastewater components.

**SURFACTANT ISSUES.** The surfactant Igepon was the active ingredient in NASA Whole Body Shower Soap, the personal cleanser specified in the 2004 and 2006 ersatzes and in early editions of the BVAD. Igepon, now marketed as Geropon TC-2, is manufactured by Rhodia. Its chemical identity is sodium methyl cocoyl taurate (alternatively, sodium methyl coconut-acid taurate) Recently a new personal cleansing surfactant has been adopted for ISS/STS, a modified version of the commercial products No-Rinse Shampoo® and No-Rinse Body Wash® which are designed for waterless cleansing of hair and skin respectively. No-Rinse’s

NASA formulas are based on a blend of commercial surfactants manufactured by Lubrizol, Sulfochem B-NBB, also known as Sulfochem B-NBBQ. The blend contains PEG-80 sorbitan laurate, cocamidopropyl betaine, sodium trideceth sulfate, glycerin, disodium lauroamphodiacetate, PEG-150 distearate and sodium laureth-13 carboxylate. The NASA formulas are adapted from the commercial formulas but use a different surfactant and lack some minor ingredients present in the COTS product. Alternative waterless Russian shampoo formulations of unknown composition have been described by US astronauts (9) and in a research report (10).

The surfactant level in the 2004-2006 ersatzes assumes that the use of personal cleansing surfactants will match the estimated usage rate of 7.13 g/crewmember-day (as NASA Whole Body Shower Soap with a nominal composition of 60% water, 40% surfactants) (5) although our sample of Igepon tested at 33.4% non-volatiles. According to the manufacturer, Sulfochem B-NBBQ consists of 42–45% of a surfactant blend containing around 6% glycerin. In our ersatz formulations both Igepon and Sulfochem were assumed to consist of 60% water and 40% surfactant or surfactant blend. However, it is not known if the usage rate of products based on Sulfochem and other surfactants will match the historical data for Igepon use in conventional shower, hairwash and handwash contexts.

Data from ISS cargo records (Charles Verostko, personal communication) indicates that typical usage rates for No-Rinse products on ISS are 64 oz shampoo per crewmember per year and 20 oz handwash per year for a 3-person crew. At a concentration of 4% surfactant in the shampoo, and 8% in the handwash, this rate amounts to around 0.22 g surfactant/crewmember-day. The two usage rates are drastically different, but it should be noted that they are not directly comparable. The Igepon usage rate was measured for body cleansing and handwashing by volunteer donors at full gravity. The ISS figure represents shampooing and handwashing in microgravity and does not include crew use of hygiene wipes and pre-moistened towels nor any Russian liquid shampoo or cleansers.

A test of hygiene water concentration is now in preparation at Johnson Space Center, using donated composite hygiene water. The surfactant use rate in this test is approximately equivalent to 1.7 g mixed surfactants/crewmember-day of which >95% is derived from No-Rinse (Audry Almengor, personal communication)

**URINE PRETREATMENT ISSUES.** - Unless urine is to be processed immediately upon collection, some form of pretreatment is necessary to stabilize it against microbial spoilage and to prevent escape of any ammonia

released from urea hydrolysis. The current American pretreatment includes an acid, since acidification traps ammonia by retaining it in solution as non-volatile ammonium ions; an oxidizer, intended to convert low molecular weight volatile organics to more soluble, less volatile forms, and an antimicrobial since acidified, oxidized urine is still able to support bacterial and mold growth over the long term. (11) Two pretreatments are currently used aboard ISS.

The “American pretreatment” uses Oxone® as oxidizer, sulfuric acid as acidulant and potassium benzoate for its antifungal properties. Oxone, manufactured by DuPont, is a triple salt  $2(\text{KHSO}_5) \cdot (\text{KHSO}_4) \cdot (\text{K}_2\text{SO}_4)$  which releases active oxygen upon breakdown and also contributes acidity through the breakdown product potassium acid sulfate ( $\text{KHSO}_4$ ). The pH of American pretreated urine ranges from 2 to 2.4 with 2.4 as the target pH value.

The current Russian sulfuric acid/chromium pretreat (12) is a liquid containing 36.5%  $\text{H}_2\text{SO}_4$ , 9%  $\text{CrO}_3$  and 54.5% deionized water by mass, which is metered into urine at the point of collection at a rate of 16.7 mL/L urine. Flush water is added at a rate of 250 to 300 mL/L urine (13). The table entries below were computed from a measured density of 1.37 for the pretreat liquid. The pH of Russian pretreated urine ranges from 1.4 to 1.8. (12)

Table 1. Urine Pretreatments

| Oxone (American) Pretreatment   |           |
|---------------------------------|-----------|
| Additive                        | g/L urine |
| $\text{H}_2\text{SO}_4$         | 2.28      |
| Oxone®                          | 5         |
| Potassium benzoate              | 1         |
| Flush water                     | 270       |
| Chromium (Russian) Pretreatment |           |
| Additive                        | g/L urine |
| $\text{H}_2\text{SO}_4$         | 8.36      |
| $\text{CrO}_3$                  | 2.06      |
| DI water in pretreat            | 12.7      |
| Flush water                     | 253       |

Both pretreatments render the urine and the mixed wastewater highly acidic, and both result in essentially the same mass and volume of treated urine. On ISS, double containment is required for oxone-pretreated urine and triple containment for chromium-treated urine (12). Removal of water from either of these pretreated urine formulations leaves highly acidic brines which can be dried down to residues with pH values lower than 0.5 as measured in our laboratory. Since sulfuric acid is a liquid at room temperature, pretreated urines do not dry to a solid but remain a thick, aggressively acidic paste.

At this writing, a SBIR project is underway to develop pretreatment strategies using safer materials.

## ERSATZ CALCULATIONS

CONCENTRATION AND VOLATILITY - Henry's law, which describes the vapor pressure of a dilute solute in a solvent, is given by

$$k_H = \frac{c_i}{p_i} \quad (1)$$

where  $p_i$  is the partial pressure of species  $i$  in the headspace,  $c_i$  is the concentration of  $a$  in the solvent, and  $H$  is the Henry's Law constant, commonly expressed in units of (mol/L)/atm. For solutes which reversibly hydrate (for example  $\text{CO}_2 \leftrightarrow \text{H}_2\text{CO}_3$ ) or dissociate (such as weak acids and bases), the Henry's Law constant is defined only for the species capable of volatilization. This definition renders the constant independent of pH. The lower the value of  $k_H$ , the more volatile the solute.

The Henry's Law constant is in fact *not* a constant, but varies strongly with temperature because temperature sets the saturation partial pressure of the solute. The temperature dependence of  $k_H$  can be found by analogy to the Clausius-Clapeyron equation and is given by

$$k_H(T) = k_H^\circ \frac{p(T^\circ)}{p(T)} = k_H^\circ \exp\left(-\frac{\Delta h_{\text{soln}}}{R} \left(\frac{1}{T^\circ} - \frac{1}{T}\right)\right) \quad (2)$$

where  $k_H^\circ$  is the Henry's Law constant at standard conditions ( $T^\circ = 298^\circ\text{K}$ ),  $p(T)$  is the partial pressure of the volatile solute at temperature  $T$  and  $\Delta h_{\text{soln}}$  is the enthalpy of solution of solute vapor in the solvent, approximately equal and opposite to the solute's enthalpy of vaporization.

Volatile weak acids and bases show an apparent pH dependence of the Henry's Law constant, based on the degree of dissociation as a function of pH. The ionized form of the solute is considered non-volatile; the non-ionized portion is volatile and behaves according to equation 1. Acids are more volatile at low pH and bases at high pH. Consider a weak acid and a weak base which ionize according to the stoichiometry



The volatile non-ionized fractions of the acid and base are respectively given by:

$$\frac{c_{AH}}{c_{A,\text{tot}}} = \frac{1}{1 + 10^{(pH - pKa)}} = \frac{1}{1 + K_A/H^+} \quad (3a)$$

$$\frac{c_B}{c_{B,\text{tot}}} = \frac{1}{1 + 10^{(pKa - pH)}} = \frac{1}{1 + H^+/K_A} \quad (3b)$$

where  $c_{A,\text{tot}}$  and  $c_{B,\text{tot}}$  are the total concentration of the acid or base in both its forms, and  $pKa$  is the acid dissociation constant. Hence an effective pH-adjusted Henry's Law constant is given for acids and bases, respectively, by

$$k_{H,\text{eff}} = k_H \frac{c_{A,\text{tot}}}{c_{AH}} = k_H \left(1 + K_A/H^+\right) \quad (4a)$$

$$k_{H,\text{eff}} = k_H \frac{c_{B,\text{tot}}}{c_B} = k_H \left(1 + H^+/K_A\right) \quad (4b)$$

These modifications of the Henry's Law constant may be combined with a mass balance equation to predict the removal of volatiles from brines during evaporative concentration at non-standard values of pH and temperature and for the desired degree of concentration.

Let  $m$  be moles of solute in the system,  $w$  moles of water in the system, and  $V$  the system volume in liters. Then the concentration of solute  $c = m/V$ . For dilute solutions in water, which has molar mass 18 g/mol and density 1000 g/L, the volume of the solution can be approximated by the volume of water present in it, so that  $V = 18w/1000$ .

The gas phase may be assumed ideal, so the ratio of the partial pressures of water and solute is equal to the ratio of their molar rates of removal from the liquid during evaporation.

$$\frac{dm}{dw} = \frac{p_m}{p_w} = \frac{c}{k_H p_w} = \frac{1}{k_H p_w} \left(\frac{m}{V}\right) \approx \frac{1}{k_H p_w} \left(\frac{1000m}{18w}\right) \quad (5)$$

In dilute solutions water, the solvent, follows Raoult's law:  $p_w = x_w p_{w,\text{sat}}$  where  $p_{w,\text{sat}}$  is the saturation pressure of pure water. For concentration of pretreated urine (approx. 32.7 g solutes/L or 0.576 mol dissociated solutes/L) to 20% solids, using Putnam's (7) correlation for the density of pretreated urine, the mole fraction of water  $x_w$  begins at 0.99 and ends at 0.926. During most of this process the solution remains dilute, so we approximate  $p_w$  by the saturation pressure of pure water.

Subject to this simplifying approximation, the variables in the above equation are now separated and integrated from initial conditions ( $m_0$  moles solute,  $w_0$  moles water) to relate the residual mass of solute to the residual mass of water.

$$\int \frac{dm}{m} = \frac{1000}{18k_H p_{w,\text{sat}}} \int \frac{dw}{w} \quad (6)$$

$$\frac{m}{m_0} = \left(\frac{w}{w_0}\right)^{\frac{1000}{18k_H p_{w,\text{sat}}}} \quad (7)$$

A spreadsheet was developed from equations 1-8 to take as inputs the average pH of a solution during concentration, the processing temperature, and the fraction of water removed ( $1 - w/w_0$ ) and calculate the residual amounts of given volatiles in the residue or brine, using Henry's Law constants from Rolf Sanders' online compilation (14). Values of the Henry's Law constants for selected volatiles are given in Table 2.

Table 2: Henry's Law Data for Wastewater Ersatz Volatiles

| Component                | $k_H$ ,<br>mol/L-atm | Ionization<br>type** | pKa   | $K_a$       | $-\Delta h_{\text{soln}}/R =$<br>$d(\ln k_H)/d(1/T), ^\circ\text{K}$ |
|--------------------------|----------------------|----------------------|-------|-------------|----------------------------------------------------------------------|
| Acetic Acid              | 5.50E+03             | acid                 | 4.76  | 1.7378E-05  | 6300                                                                 |
| Benzoic Acid             | 1.90E+04             | acid                 | 4.19  | 6.45654E-05 | 6500                                                                 |
| Benzyl Alcohol           | 9.00E+03             | acid                 | 15    | 1E-15       | 7300*                                                                |
| Ethanol                  | 2.20E+02             | acid                 | 16    | 1E-16       | 6500                                                                 |
| Acetone                  | 2.90E+01             | acid                 | 19.3  | 5.01187E-20 | 4800                                                                 |
| Caprolactam****          | 3.10E+04             | acid                 | 16    | 1E-16       | 7000*                                                                |
| Phenol                   | 1.90E+03             | acid                 | 9.9   | 1.25893E-10 | 7300                                                                 |
| N,N Dimethylformamide*** | 4.40E+01             | base                 | 10.68 | 2.0893E-11  | 7000*                                                                |
| Ethylene Glycol          | 4.00E+06             | acid                 | 14.22 | 6.0256E-15  | 7000*                                                                |
| 4-Ethyl Morpholine       | 2.40E+03             | base                 | 7.57  | 2.69153E-08 | 7000*                                                                |
| Formaldehyde             | 3.20E+03             | acid                 | 13.4  | 3.98107E-14 | 6800                                                                 |
| Formic Acid              | 5.20E+03             | acid                 | 3.75  | 3.98107E-14 | 5700                                                                 |
| Lactic Acid              | 7.00E+07             | acid                 | 3.08  | 1.77828E-04 | 7000*                                                                |
| Methanol                 | 1.90E+02             | acid                 | 15.5  | 3.16228E-16 | 5400                                                                 |
| 1,2-Propanediol          | 3.00E+08             | acid                 | 14.9  | 1.25893E-15 | 7500                                                                 |
| 2-Propanol               | 8.90E+01             | acid                 | 17.1  | 7.94328E-18 | 7500*                                                                |
| Propionic Acid ^         | 5.70E+03             | acid                 | 4.87  | 1.34896E-05 | 6000                                                                 |
| Water (for reference)    | 1.78E+03             | acid                 | 14    | 1E-14       | 5235.11                                                              |

\*Values of  $-\Delta h_{\text{soln}}/R$  are estimated from data for similar compounds, or assigned a value of 7000 if no data is available.

\*\*The acid ionization type is volatile at low pH, non-volatile at high pH. The base ionization type is the reverse. Neutrals are grouped with acids.

\*\*\*Under acidic conditions N,N-dimethyl formamide breaks down into formic acid and dimethylamine; Henry's Law coefficients reflect the diethylamine.

\*\*\*\*A pKa of 16 was assigned to neutral caprolactam.

#### COMPOSITIONAL SHIFTS UPON CONCENTRATION –

The figures below show the model results for normalized aqueous phase concentrations of three dilute solutes as the solution is evaporated to an endpoint of 98% water removal. Acetic acid is a volatile weak acid; ethanol, a neutral volatile; and dimethylamine is the volatile weak base formed upon breakdown of N, N-dimethyl formamide. The four graphs of Figure 1 show the patterns of solute removal over a range of pH values from pH 2 to pH 9.

The effective volatility of acids is highest at low pH, where the acid molecules appear in solution chiefly in the neutral/protonated form. As a rule of thumb, removal of 95% of the water at pH 2 removes 60 to 70% of volatile fatty acids (formic through octanoic).

Bases such as dimethylamine (shown) and ammonia are most volatile at high pH as shown in the graph for pH 9.

The volatility of neutral, non-ionizing compounds is independent of pH. Alkane-series alcohols found in humidity condensates (e.g. methanol through butanol), ketones such as acetone, and hydrocarbons have relatively low values of  $k_H$  ( $k_H < 100$ ) and are readily removed during evaporative pre-processing, being quantitatively captured in the condensate.