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E. I. DU PONT DE NEMOURS & CO., INC.
COMPANY CONFIDENTIAL

TECHNICAL REPORT

PERFLUORO OCTANOIC ACID CONCENTRATION(C8) IN WASTE WATER

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PREVIOUS RELATED REPORTS: SpAR 79-3, SpAR 82-1, TR 82-1

PROJECT CODE: N/A

PERIOD COVERED: 9/91 - 12/91

NOTEBOOKS COVERED: N/A

ABSTRACT

The company as set a CEG (Community Exposure Guideline) of 1 ppb in water for ammonium pefluoro octanoate (C8), a surfacant in the Teflon* dispersion used to produce Teflon* fiber. A conservative position of assuming all C8 ends up in the James River would produce an average concentration of 0.1 ppb. The only time the CEG could be exceed would be during periods of extreme low flows in the river.

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INTRODUCTION

Teflon* dispersion is made in Parkersburg, WV at Washington Works. Ammonium perfluoro octanoate is a surfacant added to the dispersion to prevent aggolmeration of particles. Ammonium perflucro octanoate is commonly call C8. This compound has been found in the groundwater around Washington Works.

An examination of previous technical studies and samples of waste water streams were analyzed to evaluate the any potential community exposure. CH2M Hill's laboratory was contracted to analyze waste water streams for C8. The results could only account for 50% of the C8. Surrogate recoveries on known amounts added to distilled water were from 52% to 86%. The possibility of the test being in error by a factor of two is real. The conservative approach is to assume that all of the C8 ends up in the plant's waste water system.

At average Teflon* fiber production rate along with the average James River flow (5104 MM gpd), the C8 concentration would be 0.10 ppb. Maximum fiber production could raise the level to 0.15 ppb. Extreme low flow in the river could raise the concentration of C8 in the river above the 1 ppb limit. The river flow would need to drop below 1000 MM gpd. The low flow for the James River on a repeatable 10 year cycle (7Q10) is 408 MM gpd. During periods of extreme low flow in the river, the production of Teflon* fiber may need to be curtailed so as not to exceed the the company's CEG of 1 ppb.

PROGRAM OBJECTIVES

1. To determine what happens to C8 in the Teflon* spinning process.

2. Establish the extent, if any, of community exposure to C8 caused by the site's waste water.

RESULTS & CONCLUSIONS

1. The analysis for C8 does not allow for doing an accurate mass balance. The test is believed to be ~50% accurate. About 95% of the C8 is to believed to exit the process with the wash water and the remaining 5% condenses in the exhaust system and exits with the effluent.

2. At normal river flow, 5104 MM gpd, the maximum C8 concentration possible in the James River should not exceed 0.15 ppb.

3. Production may need to be curtailed when the James River falls below 1000 MM gpd so that the C8 concentration does not exceed 1 ppb in the river.

RECOMMENDATIONS

1. No further testing for C8 be done at this time.

PATENT SITUATION

No patent action has been taken or is anticipated as a result of this work.

PUBLICATION STATUS

No publications are planned.

SPECIAL SAFETY PRECAUTIONS

Normal SOP's cover all of tahis work.

ENVIRONMENTAL CONSIDERATIONS

Stay abreast with Washington Works efforts around dealing with C8 in the workplace atmosphere and in ground water.

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I Introduction

Teflon* colloidal dispersion is mixed with viscose in the manufacture of Teflon* fiber. The cellulose contained in the viscose is regenerated in the coagulation/acid bath in spinning. The regenerated cellulose acts as a matrix to bind Teflon* particles prior to sintering. Surfactants are used in the manufacture of colloidal Teflon* dispersions to prevent agglomeration of particles One of the sufactants used is F-143, ammonium perfluoro octanoate (commonly referred to as C8).

2. DISCUSSION

A. EARLIER ISSUES

In 1978, the 3M Company notified DuPont that C8 used in Teflon* polymerization may be teratogenic. Airborne dust or vapors were felt to be the source of the exposure Several technical projects(Reports SpAR 79-3, SpAR 82-1 & TR 82-1) were initiated to study the potential exposure to C8 by DuPont employees. C8 was not detected in the work place air environment The handling of coated packing yarns or direct contact with Teflon* dispersion were the only potential areas that personnel can be exposed to significant levels of C8 (Ref. 4). Tests at Haskell Lab showed no transfer of C8 from yarns to rabbit skin and suggested C8 exposure of persons handling dry yarn is minimal (Ref 5) C8 was later determined not to be teratogenic by 3M and DuPont's Haskell Labs.

B. TEFLON* DISPERSION

Teflon* dispersion is produced in a batch operation at Washington Works. C8 which is the ammonium salt of perfluoro octanoic acid is used as a wetting agent to prevent agglomeration of the Teflon* particles. A batch of dispersion is initially about 7000 lbs which contains 3000 lbs of Teflon* monomer A total of 4060 grams of C8 is added to the batch in the precharge and injection steps. After polymerization is compoleted, the dispersion is decanted to obtain 60% solids. Washington Works estimates that 50% of the C8 is removed with the decanted supernate and the other 50% goes with the concentrated dispersion On a Teflon* solids basis, the C8 concentration would be 1490 ppm, and 900 ppm on a dispersion basis.

The Teflon* dispersion (T 3311) used for fiber production is pH adjusted with sodium hydroxide which changes the C8 from an ammonium salt to a sodium salt. In the coagulating/acid bath used in Teflon* fiber spinning, the C8 will convert to the acid form, perfluoro octanoic acid.

C. PREVIOUS CONCERNS

Previous research examined employee potential exposure to C8 through handling of yarn. Sintered Teflon* yarn had non-detectable levels of C8 (Ref. 4) The Teflon* fiber sintering temperature is 325 C.

The boiling point of perfluoro octanoic acid is 188 C. Yarns with a Teflon* coating, which are not exposed to high temperatures did contain detectable levels of C8. Thermal treatment of these yarns was effective in removing the C8. The research showed that the C8 removal was a function of time and temperature (Table 1),(Ref. 2). IR scans of off gas from the heated yarn samples provided the basis for the conclusion that the C8 decarboxylates into CO2 and perfluoro monohydride and does not evaporate as it is heated up to 200 C (Ref. 4).

The data follows the kinetic "rule of thumb" that increasing the temperature 10 C produces a doubling of the rate Extrapolating this relationship up to the sintering temperature of Teflon* predicts that all the C8 is removed from the fiber.

D. PRESENT ENVIRONMENTAL CONCERNS

The present environmental concerns with C8 are with ground water contamination A CEG(Community Exposure Guidelines) of 1 ppb in water has been established by Haskell Labs.

Samples of effluent from different spots in the Teflon* spinning process were taken to estimate the concentration of C8 in the site's waste streams. Sample locations are listed in Appendix I.

CH2M Hill was contracted to analyze the samples A summary of their results are in Appendix I. A complete report from CH2M Hill is contained in Appendix II. The sample results do not allow for a complete mass balance. The measured concentrations in the effluent streams only accounts for about 50% of the C8,(Fig. 1 & 2). There are several possible explanations, the initial C8 concentration is 750 ppm on a dry Teflon* basis, the C8 chemically reacts, it is encased in the yarn, it decomposes, evaporates or the reported levels are in error low The lower initial C8 concentration is not likely because of independent analysis done by Washington Work and Spruance have measured the concentration at about 1000 ppm on a dispersion basis The C8 will change to perfluoro octanoic acid in the bath which should not react with the normal contents of the Teflon* spinning acid bath. There is no reasonable way to prove the idea of C8 being incased in the yarn.

Previous work measured C8 on unsintered Teflon® yarn at 60ppm (Ref. 4). The concentration would need to be 700 ppm to account for the missing C8. The previous work concluded that the C8 carried with the unsinterred Teflon* yarn would decompose during the sinterring process. This is in contradition to Washington Works process of recovering C8 from their "fine powder" exhaust stream.

"Fine powder" Teflon* has been tested and found to contain little or no C8. The "fine powders" are dried at 190 C. Washington Works recovery of C8 from the "fine powders" exhaust contradicts the previous conclusion about decarboxylation versus evaporation. If C8 evaporates off the yarn in the fiber spinning process, it should condensed in the spinning exhaust system. To reduce the potential for a duct fire, water is sprayed in the exhaust hood to reduce the temperature down below 65 C. The exhaust gas then passes through a wet scrubber and the final gas temperature is basically reduced to ambient conditions. The water drained from the exhaust hood and the scrubber go into the Teflon* basement east floor trench. If all of the C8 eventually ends up in the sewer, this would lead to the conclusion that the analysis from CH2M Hill are low.

CH2M Hill ran surrogates on three samples. Surrogate recoveries were not determined on the high concentrated samples due to the large dilution required for analysis. Surrogates were run on the discharge from the exhaust scrubber and two distilled water samples, one sent by Spruance and one from CH2M Hill's lab. The exhaust scrubber effluent was analyzed to have 1.8 ppb of C8, and the detection of known amounts of surrogate material added was less than 50%. The explanation for the low surrogate recovery was due to the noise created by a large non-target chromatographic peak coupled with a large dilution factor. Decomposition products of cellulose that are scrubbed out of the exhaust gas are the mostly likely cause of the non-target chromatographic peak. The surrogate recoveries on the distilled water samples ran from 52% to 86%. The possibility of the analysis being low is real.

There is alot of contradicting material on the fate of C8 in the Teflon* spinning process. The belief that CH2M Hill's results are low by a factor of ~2X would tie together the majority of the material. The 60 ppm measured concentration of C8 on the yarn only accounts for ~5% of the total material. The other 95% exits the process in the wet portion of the spinning process, the washing step since the acid bath is 100% recycled. The 5% on the yarn evaporates and then condenses in the exhaust hood similar to Washington Works recovery process. Only trace amounts of C8 should reach the scrubber. The amount found in the exhaust scrubber was less than 0.02% of the total amount.

If 95% of the C8 exists the process with the wash water, the concentration of SM #2 sample should have been 4600 ppb CH2M Hill's measured amount of 2400 ppb is 52% of that level. This percentage is in the range of report surrogate recoveries on distilled water.

The most conserative positon in estimating the potential environmental impact is to assume that all of the C8 ends up in the plant's waste effluent. This would about double all of CH2M Hill's measured concentrations (Fig 3 & 4).

During the sampling period 11/13 & 11/14/91 and estimated 1194 grams/day of C8 were discharge to the James River. The long term average(1937 to 1987) flow for the James River is 5104 MMgpd. This would make the C8 concentration in the James River an estimated 0.06 ppb.

The average annual production rate for Teflon* fibers is 1 MM lb. This would discharge 1490 lb of C8 to the James River annually. The estimated C8 concentration in the river would be 0.10 ppb. The maximum production rate for Teflon* fibers is 4200 lb/day. This could add 6.3 lbs C8/day to the James River and produce an estimated C8 concentration of 0.15 ppb in the river.

The low flow in a 10 year repeating cycle (as defined by 7Q10) for the James River is 408 MMgpd. An average production rate during this period would produce an estimated C8 concentration in the James River of 1.20 ppb and maximum production rates would increase the concentration to 1.84 ppb. During the low flow periods, which should happen once every 10 years, production may need to be curtailed to 2300 lb/day of Teflon* fiber to stay below the CEG of 1 ppb.

REFERENCES

1. Forte, M.A. - SpAR 79-3

2. Forte, M.A., Mokhtar, A.M. - PCD Monthly, June, 1981

3. Shelburne, S.S. - PCD Monthly, December, 1981

4. Shelburne, S.S., Forte, M.A., Mokhtar, A.M. - SpAR 82-1

5. Burks, P.P., - TR 82-1

TABLE 1

THE EFFECT OF HEAT

ON EXTRACTABILITY OF

C8 FROM YARN (Ref. 2)

Initial C8 concentration on 9450 I & T yarn ~ 600 ppm

	% C8 Remaining on Yarn		
Time of Heat(minutes)	150 C	175 C	200 C
10	75	41	N/D
20	72	12	N/D
30	72	N/D	N/D
40	47	N/D	N/D

N/D Not detectable, < 5 ppm

Least Square Fit for proposed 1st Order Decarboxylation

150 C $A = Ao * e^{-0.0155t}$ (t=minutes)

175 C $A = Ao * e^{-0.106t}$ +10 C => $(0.106/0.0155)^{0.4} = 2.16$

(close to "rule of thumb" for temperature dependency of kinetic reactions, +10 C roughly doubles reaction rate)

Extrapolation to 200 C $A = Ao * e^{-0.725t}$

t= 10 , A = 0 4 ppm which is < 5 ppm minimum detectable limit

Extrapolation to 325 C (Sintering) $A = Ao * e^{-10844t}$

< 0.1 ppb at t = 0.0014 minutes ~ 0.1 seconds

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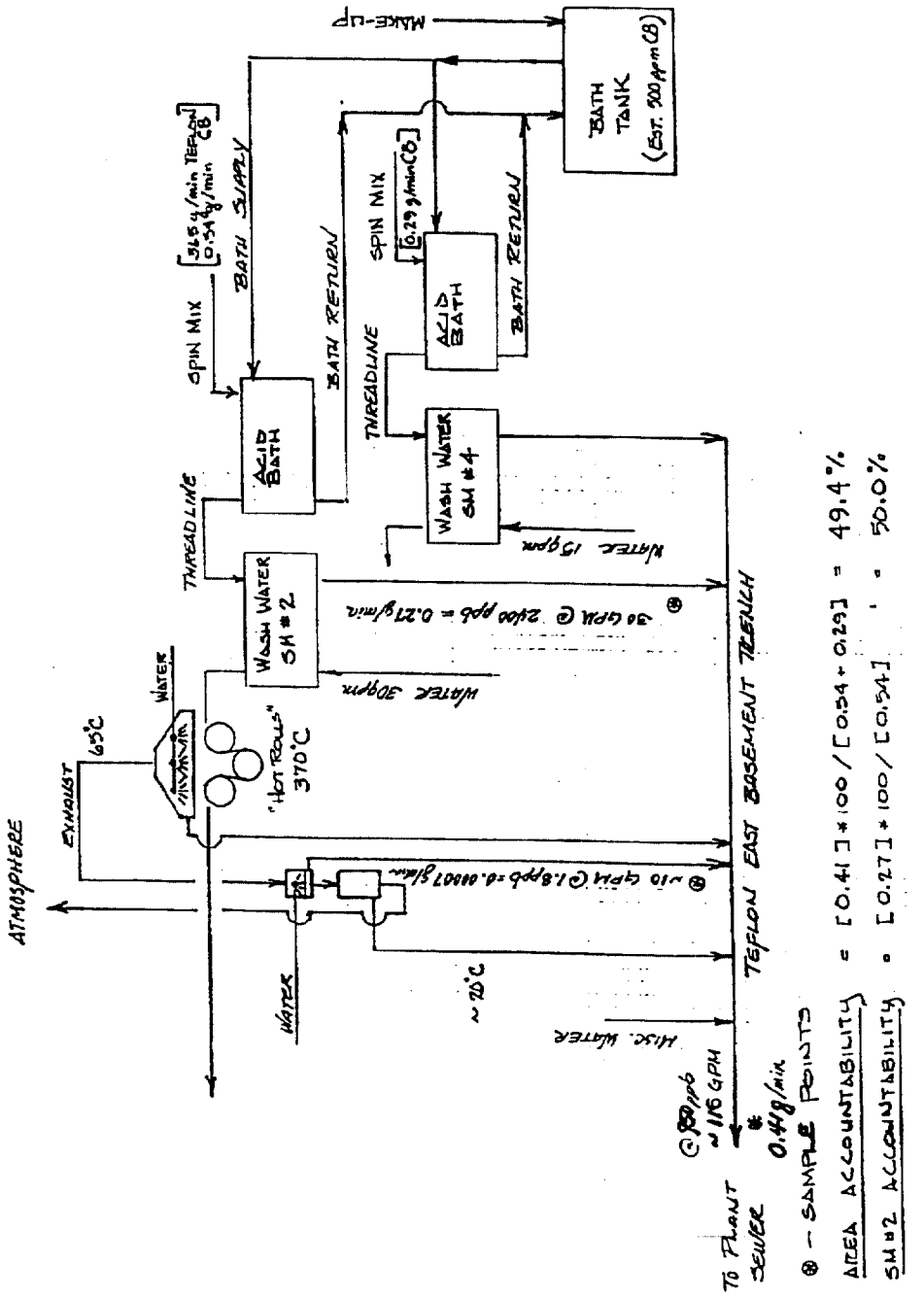
EID714260

FIGURE 1

TEFLON* SPINNING
NOVEMBER 13, 1991

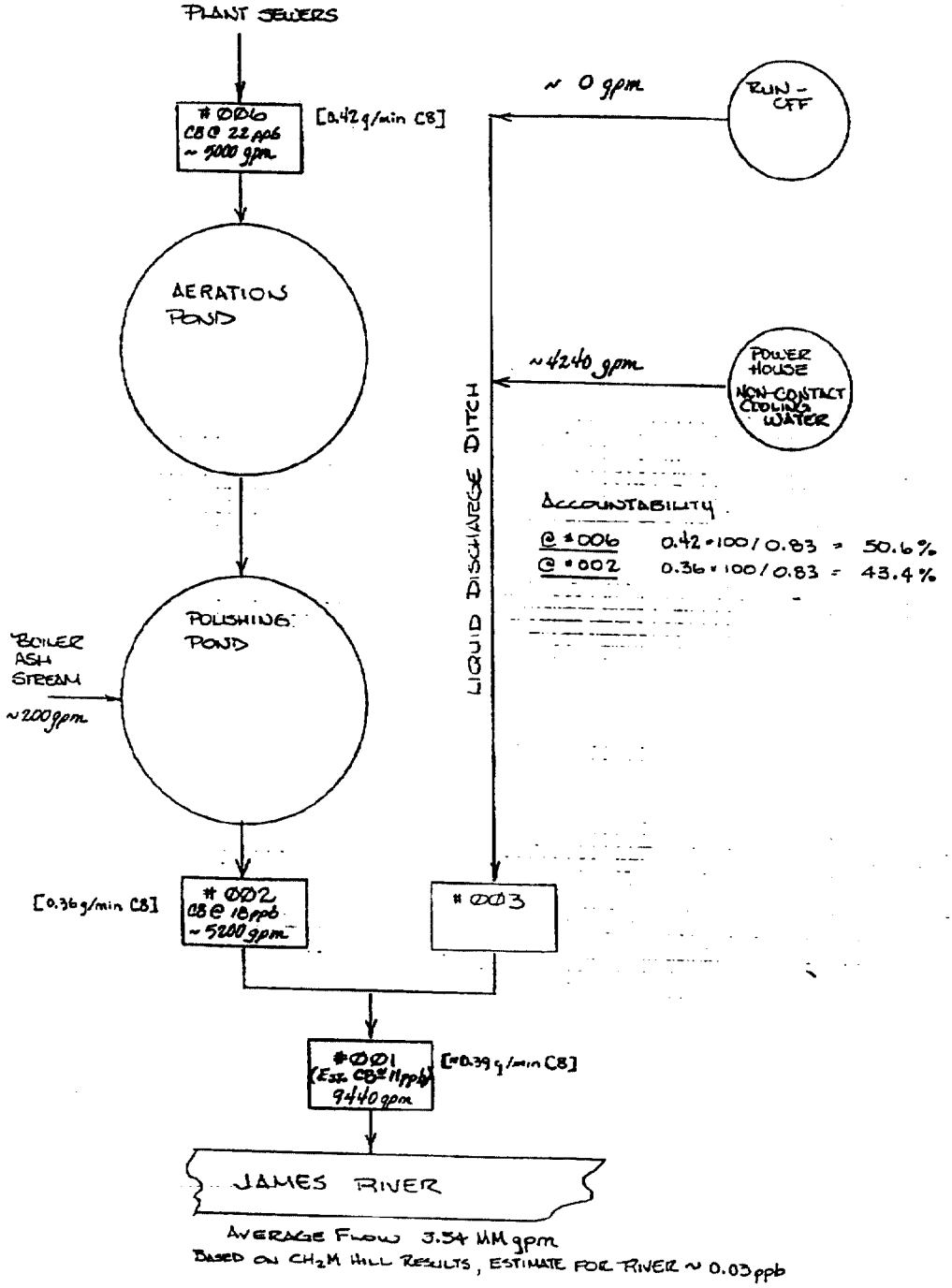


SPR000349
EID714261

FIGURE 2

MASS BALANCE OF C8 USING CH_2M HILL TEST RESULTS

SPRUANCE WASTE WATER TREATMENT SYSTEM
NOVEMBER 13, 1991



SPR000350
EID714262

FIGURE 3

PROPOSED MASS BALANCE OF C8 IN TEFLON* SPINNING

NOVEMBER 13, 1991

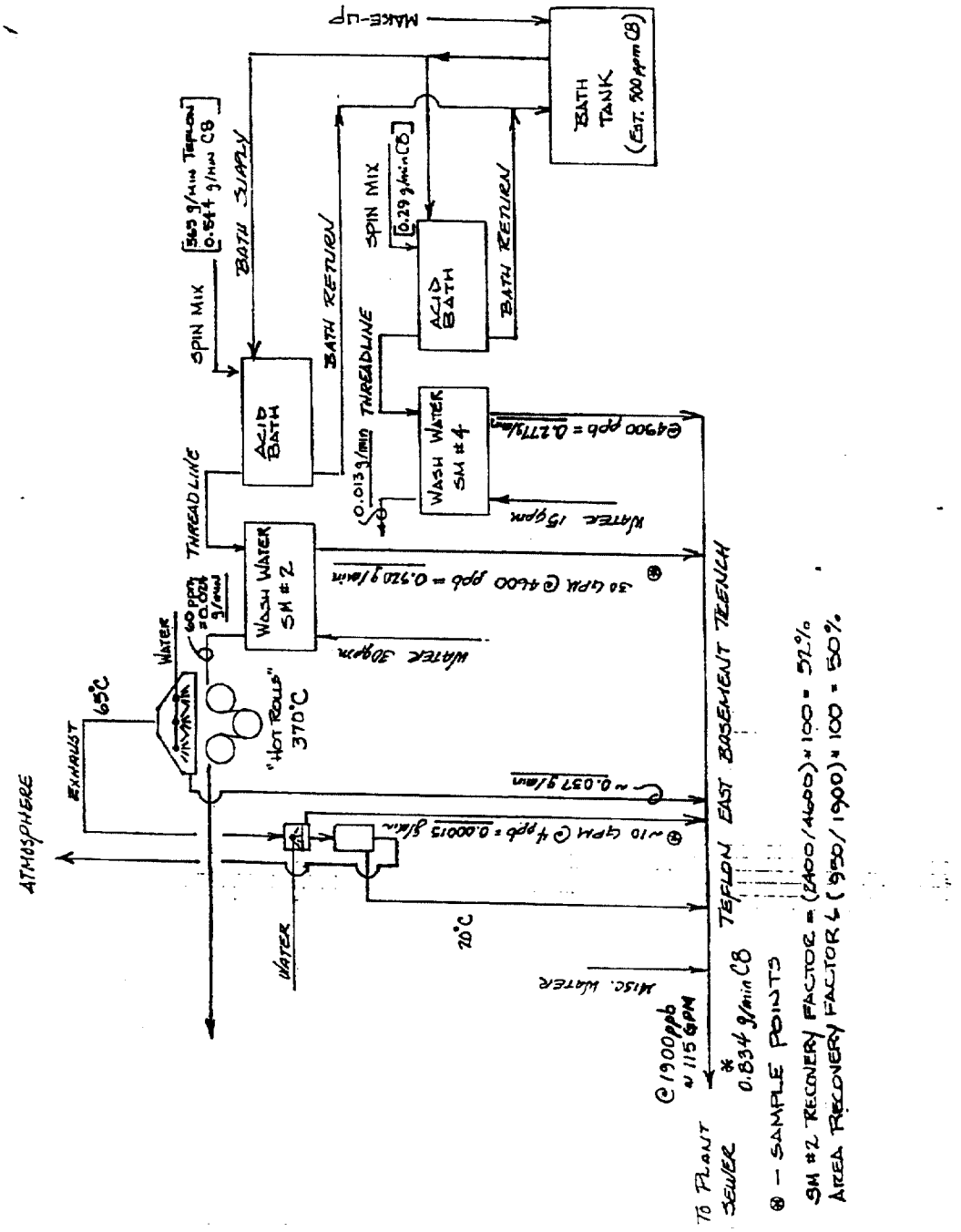


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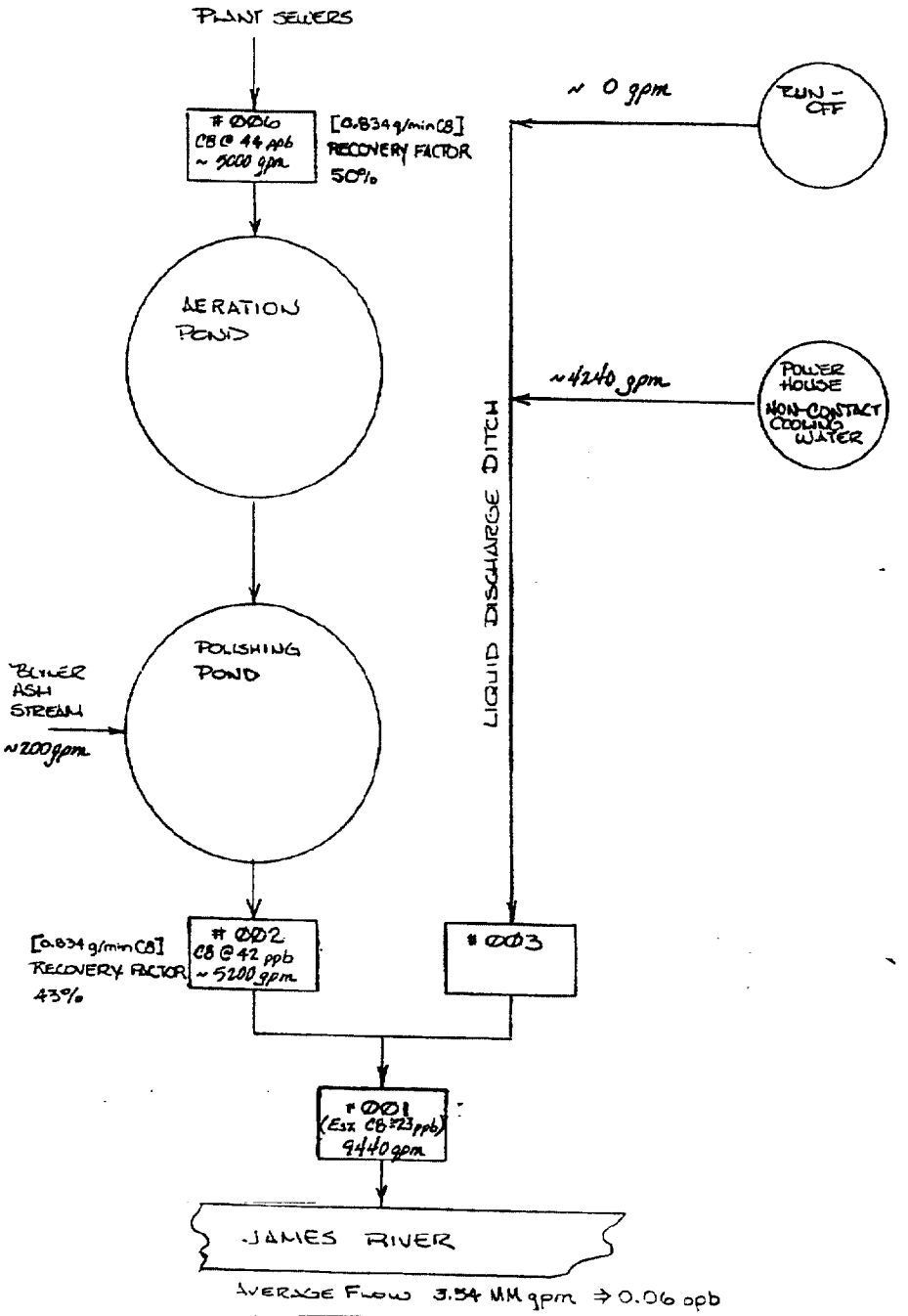
FIGURE 4

PROPOSED MASS BALANCE AROUND WASTE WATER SYSTEM

NOVEMBER 13, 1991



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