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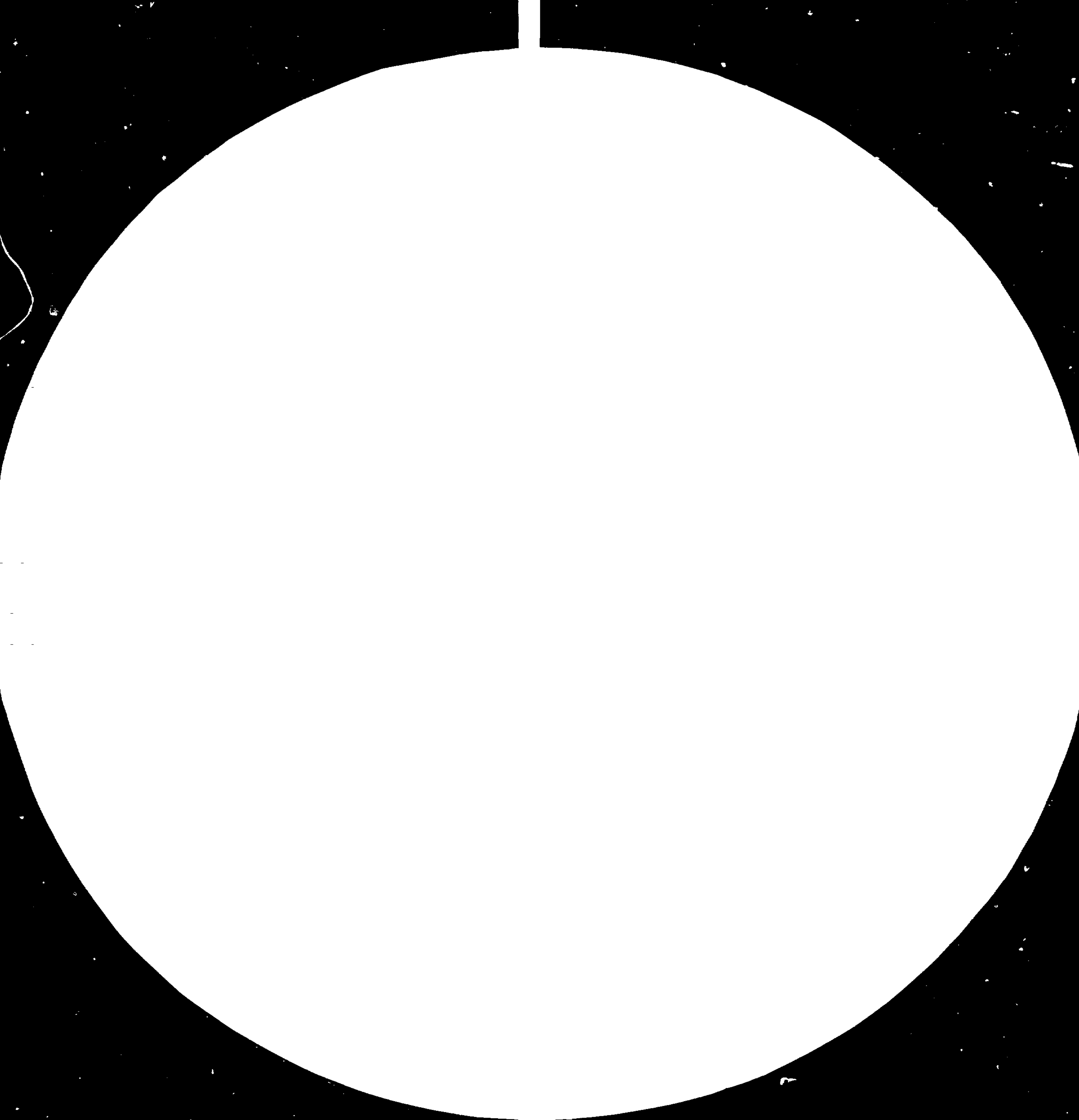

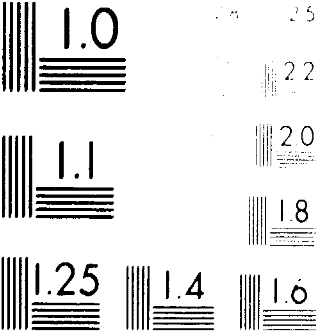
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Evaluation of Propylene Oxide Manufacturing.
HAK-I and HAK-II,
Tuzla, Yugoslavia

by
Paul E. desRosiers
UNIDO Expert
Project YUG 78/006

16 July 1981

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Preface

I can be quite frank when I relate, for the record, that I have been highly impressed by the enthusiasm and dedication of staff members from the Institute of Chemical Engineering relating to this project. There is no question in my mind that it is only through direct support from UNIDO and the UNDP that such positive research could ever occur at the scale at which I have observed here in Tuzla.

In my estimation the funds are more than well spent and serve as a catalyst not only to motivate scientists and engineers, but also to solve real-world environmental and economic problems. I am proud and quite satisfied to have had the opportunity to have participated as a UNIDO team member.

I would therefore highly recommend continuation by UNIDO of its very active support of the present projects and any future programs contemplated in this area.

Paul E. desRosiers
16 July 1981, Tuzla

Forward

I wish to thank all the members of the Institute of Chemical Engineering and staff of HAK-I with whom I spent many moments reviewing, discussing, explaining, verifying, and being educated. I wish to express my sincerest appreciation to the two interpreters, Ž. Arnautović of the Institute, and B. Čudić from HAK-I, for without the use of their knowledge and ability, I would not have been capable of performing my mission. Last of all, I want to thank deeply my hostess Mrs. P. Kovačević, who not only extended to me the opportunity to share my experiences from Love Canal, New York and Seveso, Italy with local scientists and engineers concerned with the quality of our health and environment, but provided the hospitality that made my short stay in Tuzla more enjoyable and comfortable.

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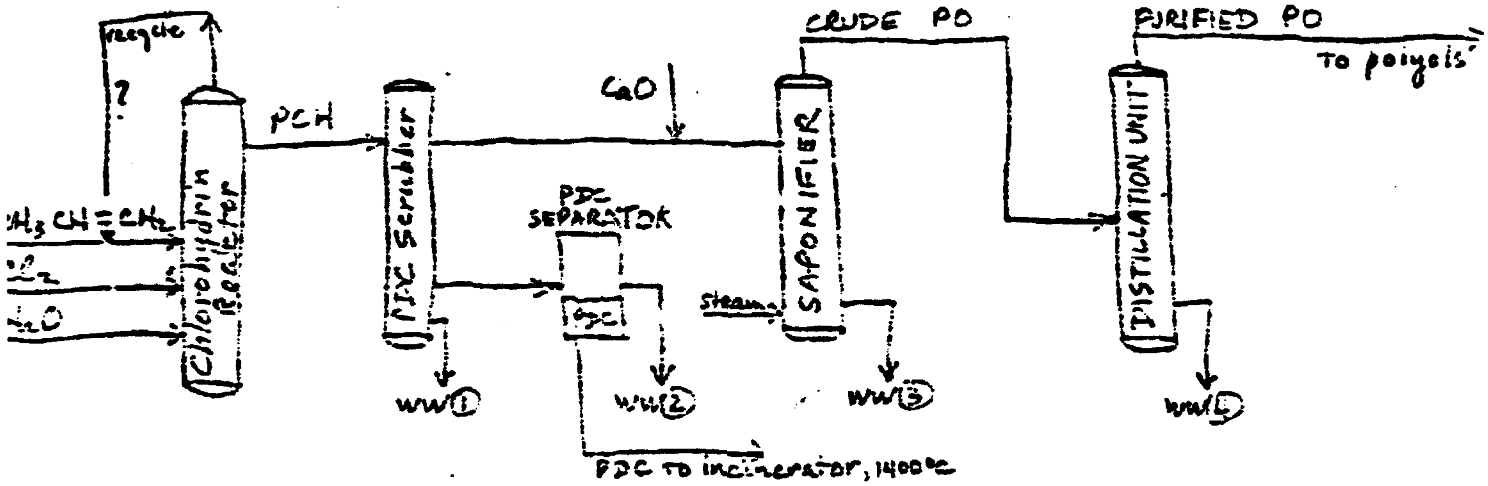
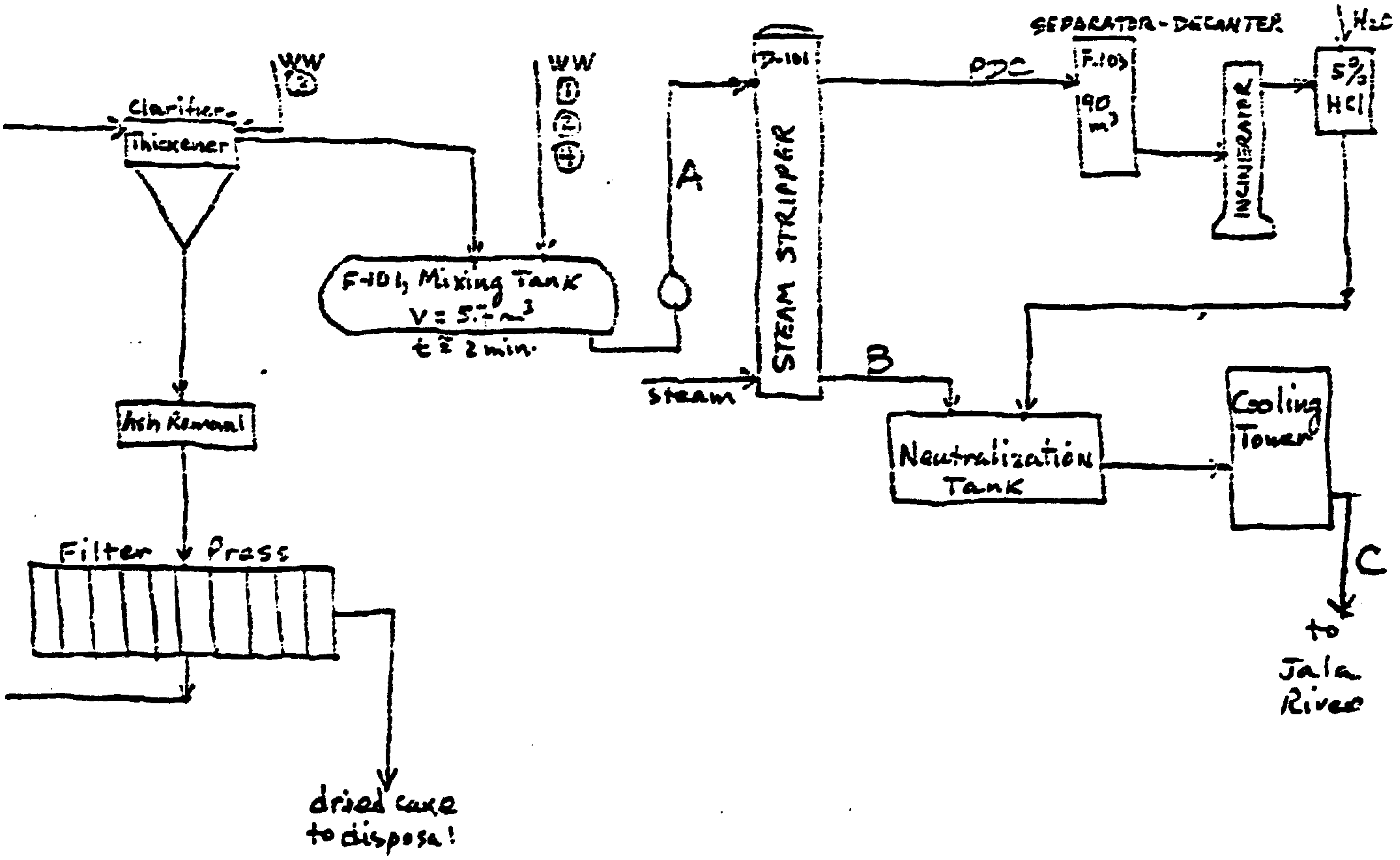
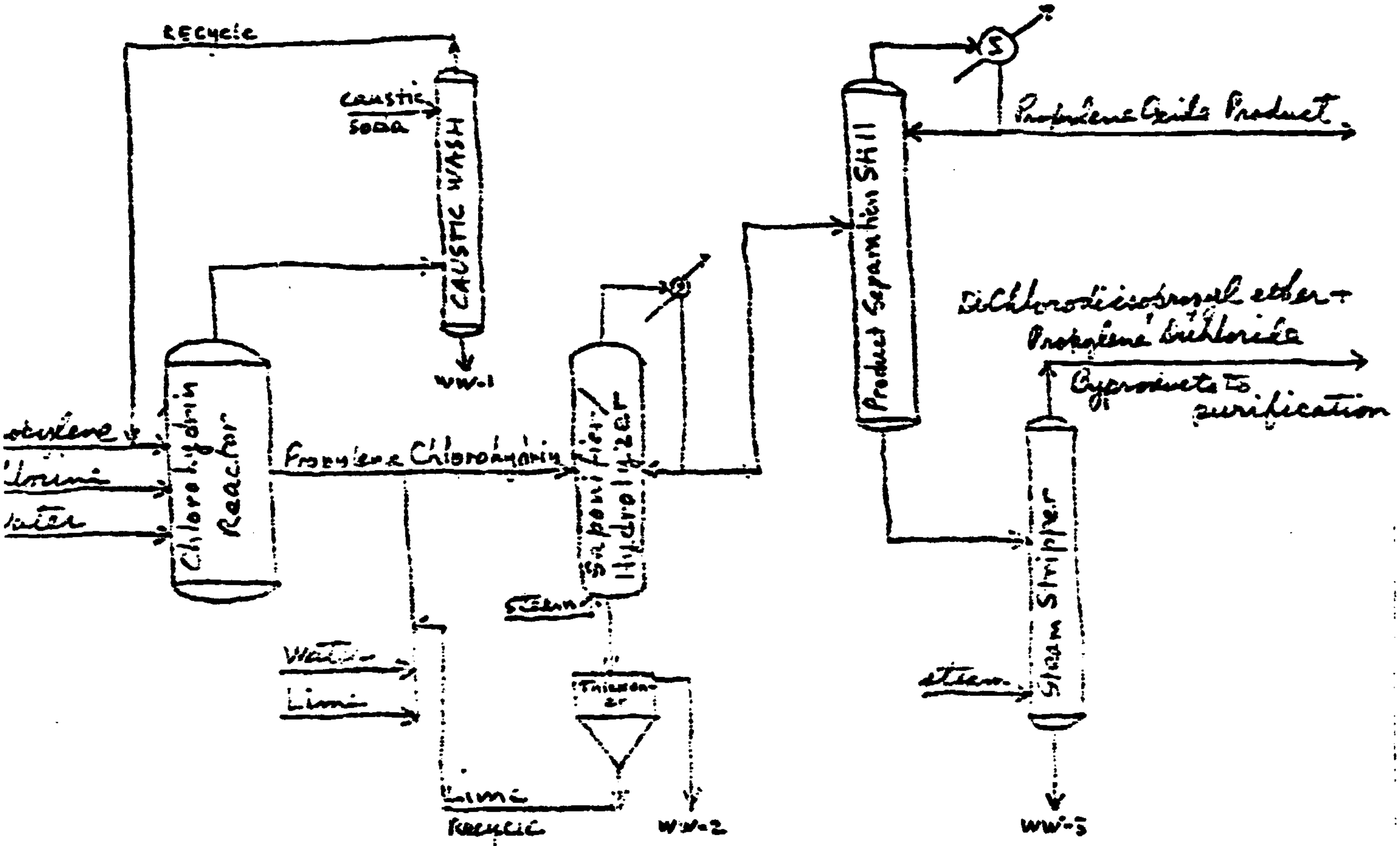
1. Propylene Oxide Process.



2. Treatment Scheme.



3. Typical U.S. Propylene Oxide Process via Chlorohydrin



Wastewater Streams -1, -2, -3 go to specialized activated sludge treatment sequence as described in Dow Chemical (Freeport, Texas) report. Lime problems, regarding Dow Chemical Co., do not exist as caustic soda, NaOH, is used in saponification. Typically, those chemical firms still using the chlorohydrin method for production of PO in U.S. recover and reuse excess lime from the thickener and use it as make-up, as shown above

4. Discussion of Individual Problem Areas:

   a. Feedstock Cleanup

      (1) Propylene - from all indications the quality of the C_3H_6 is very high, i.e., >99%; however, it is most important that constant care be taken to insure that not only the highest quality be maintained, but knowledge of the impurities, i.e., propane and other aliphatics, be recorded through proper and accurate monitoring.

(2) Water - demineralized water is provided by the Tuzla thermoelectric plant through the use of Zeolite resins, which act to "soften" the raw water and remove hardness ingredients such as scale-producing Ca^{++}, Mg^{++}, Fe^{++}, etc. I believe it is important here to provide adequate analyses for SiO_2 and other metals to insure low concentrations as many trace quantities of metals may act as undesirable catalysts in the reactor. I understand that the hardness of the presently provided demineralized water is equivalent to 40-50 mg CaO per liter.

(3) Chlorine - Again, I cannot overemphasize the importance of the highest quality chlorine and that monitoring for by-products, such as phosgene, becomes routine. Any R-Cl impurities in the feed chlorine will cause headaches later in the reaction sequence. I assume that Hg-cell brine wastes are properly treated and disposed of in such a way as to not cause any future groundwater contamination problems.

(4) Lime - I realize that HAK-I staff are acutely aware of the decrease in quality of this secondary feedstock over the last year:

	June 1980	May 1981
CaO, active	93.31	80 - 85
MgO	1.42	1.23
$CaSO_4$	1.34	
SiO_2 + insolubles	0.51	0.84
Fe_2O_3, Al_2O_3] R_2O_3	2.35	0.70
ash	1.34	4.55
SO_3	0.78	2.0

Good chemical engineering practice dictates that feedstock quality be properly maintained at the highest level at all times otherwise product quality and quantity decrease, mechanical failures in pumps (impellers, e.g.) increase, scaling and fouling of packing material increase, corrosion and abrasion increase, and last of all, pollution is enhanced and often magnified. (More will be discussed concerning this matter in the following segments in a more specific manner).

b. Quality of Lime

If the lime, presently in use, is continued to be used, then special pretreatment must be employed to remove undesirable components, such as SiO_2, ash, and also to effect a reduction in R_2O_3 and MgO. Each of the latter components must be reduced for separate reasons.

As we know, there is a rule-of-thumb in the chlorohydrin process for PO that the MgO content of the lime used must not exceed 1%, otherwise it is believed that MgO acts as an undesirable catalyst that causes propylene oxide to be converted to proprionaldehyde through an isomerization route.

Equally important, and unsubstantiated by any significant test data, is the fact that higher percentages of R_2O_3 (e.g., Fe_2O_3 and Al_2O_3) have, in my experience, acted with more importance as catalysts. Experiments should be performed to assess the catalytic effects of R_2O_3. These metallic oxides may play a more major role in side reactions than MgO.

The presence of high quantities of ash or inerts is particularly undesirable because of the potential for abrasion of impellers in pumps and vessels (due to grit and sand components).

Finally, SiO_2 is known to cause serious fouling or scaling of packing material in steam strippers. SiO_2 behaves in a particularly unwanted manner, as it becomes silicic acid at moderately low pH and silicate ion at pH greater than 9. At low pH, it precipitates out as a glass and is particularly tenacious, and at higher pH, it slimes or covers mostly everything. Once deposited, it is nearly impossible to remove, unless it has become an integral part, through occlusion, of the precipitate or deposit or scale. In the latter case, if it is admixed with $CaCO_3/MgCO_3$ scale, HCl may prove effective.

The quality of the lime, therefore, becomes seriously important when the propylene oxide process wastewater is combined jointly with the municipal wastewater, particularly in regards to the quality of the biological solids produced and their respective settling properties.

c. Thickener - Sedimentation Unit

Because a sedimentation tank is normally designed for an overflow rate of 600 - 1000 gal/day-ft^2 and a thickener for an overflow rate of 200 gal/day-ft^2 and also because of the recent significantly lower quality of the lime employed in the PO process, the sedimentation tank design capacity may be greatly overloaded. Thus, carryover of unwanted inorganic suspended solids to the steam stripper may be causing a decrease in efficiency in the stripping column as far as PDC is concerned, as evidenced from deltas or differences in 14-day operational data obtained by HAK-I on 15-5-81 and 29-5-81 compared to data obtained on 1-4-81 and 15-4-81. Scaling of the packing media undoubtedly accounted for this reduced efficiency. A materials balance for PDC (in the overheads and bottoms) together with quantity of HCl production from the incinerator would have proved this hypothesis.

Furthermore, I believe that the hydroxide alkalinity (phenolphthalein method) must be neutralized prior to Wastewater Stream -3 input to the mixing tank (discussed later).

Normally, in the U.S. industry where lime is used as the saponification agent, there is no sedimentation tank, but a thickener, which is used to concentrate the unused $Ca(OH)_2$ and separate the $CaCO_3$, $MgCO_3$ (recall that $Ca(OH)_2 + 2HCO_3^-$ alkalinity $\xrightarrow{pH > 8.3} \underline{CaCO_3} + 2H_2O$), and then the unreacted or excess $Ca(OH)_2$ is recycled as makeup with fresh lime to the saponification unit. This alternative should not be overlooked, as it results in a savings in lime requirements.

d. Mixing Tank (F-101)

The real purpose of this vessel is not only to serve as a receptacle for adding and mixing of Wastewater Streams -1, -2, and -4 with the overflow from the thickener-sedimentation tank (Wastewater Stream-3), but to serve as a quasi-equalization tank to dampen out broad variations in R-Cl pollutants to the steam stripper, so that the latter unit receives a regular or stable concentration of chlorinated organics (with high volatility) in order for the steam to vaporize these components to be collected in the overhead, enriched in PDC + DCDIPE for transport to the PDC separator-decanter tank (F-103), whereupon the PDC is removed simply by its specific gravity difference and pumped to the incinerator for conversion to HCl.

I have calculated the residence time in this mixing tank to be: $(5.7\ m^3/163.3\ m^3/hr) \times 60\ min/hr = 2\ min$. Hence, this tank, in my opinion, serves no useful purpose regarding equalization or dampening the broad fluctuations in concentrations of pollutants/contaminants fed to the steam stripper.

To reiterate what I have said earlier: any hydroxide ion present must be neutralized (recommendation - add 5% HCl just before mixing tank). This should prevent or significantly reduce liming or scaling of the packing and should increase the efficiency of the steam stripper appreciably. (Recall here the use of the Langelier Index to determine scaling potential of the wastewater stream.)

e. Analytical/Monitoring Parameters.

Upon review of the analytical data from the PO process, I noted the random absence of consistency among parameters, that I would consider to be routine. I list, in the table below, what I believe should be the parameters utilized either routinely or at a specified frequency in addition to those normally considered:

Feedstocks	Routine	Monthly	Monitoring Parameters
propylene		x	propane
water	x		TDS, hardness
chlorine	x		phosgene*, Hg^{++}
"		x	R-Cl or TOCl
lime	as necessary		MgO, R_2O_3, SiO_2, ash, $SO_3^=$
Wastewater Streams			
1, 2, 3, 4 mixed to and after stripper	x		(TOD, BOD_5, COD or TOC) SS, pH, temperature, TOCl
"		x	PDC, ECH, PCH(1,2), PG, DCDIPE, Cl^-, Ca^{++}, total + phenolphthalein alkalinity

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* Analytical method required

Selection of these parameters and subsequent analyses should provide sufficient data to judge the efficiency and effectiveness of the steam stripper. (It is apparent that the thickener - sedimentation tank effectiveness can be obtained by other means). The pH measurement, and the maintenance of the pH in the range of 6-8, is critical to the performance of the steam stripper, to minimize scaling potential.

f. Removal of Toxic Chemical Artifacts.

An artifact is an unavoidable and low concentration by-product that oftentimes causes serious problems due to its inherent high toxicity. Here, we are talking about ECH and DCDIPE. Normally, these two compounds, together with PDC, are conveniently and effectively removed by steam. However, due to some of the troubles already mentioned elsewhere, significant concentrations may end up in the steam stripper bottoms. Previous studies by Dow Chemical Co. have shown DCDIPE to be toxic to biological organisms in the 30-100 mg/l range. The upper limit causes biomass kill and endogenous respiration to ensue. The recommendation by UNIDO expert Hüber that it would appear advantageous to investigate the possible application of Amberlite RH5310, a macroreticular resin, highly specific for chlorinated hydrocarbon adsorption, appears warranted, and I concur with his good advice. Hopefully, laboratory studies will prove that this resin has a preferred affinity for trace R-Cl over PG.

g. Equalization Pond or Unit.

Some mention here should be made of the utility of some sort of equalization vessel or pond to replace the present mixing tank of minimal capacity. You seem to have before you a choice of economic trade-offs between placement of this tank before the steam stripper or before the combined industrial-municipal activated sludge unit. I believe, and I will have to give this considerably more thought, that some sort of compromise can be arrived at regarding size, but I strongly feel that there must be two equalization units, one prior to the steam stripper (its proper operation is as important to the product PO quality as to the reduction of pollutants discharged to the neutralizer) and one before the aeration basin. Elimination or minimization of suspended solids carryover will obviate the need for larger equalization units or ponds.

h. Neutralization Tank.

As with all pH probes, they are subject to the harshness of the environment into which they are placed. Proper selection of quality pH probes and replacement parts, together with constant maintenance will provide adequate life to these probes.

After observation of the tanks, however, I feel that due to the nature of the conditions there, i.e., hot wastewater and hydrochloric acid, that corrosion to electical conduits and cables and leads has taken its toll. I recommended that, in the future, the pH meter assemblies be mounted away from the top and a distance to the side of the neutralization tanks. As you realize, it is essential that remote operational control of pH be strictly maintained prior to discharge of this wastewater to the biological system.

i. Filter Press.

I have three separate comments to address regarding the filter press operation. Firstly, worker safety should be stressed through an educational program to inform the staff of the potential hazards to human health due to the chemicals present in the raw suspensions to be dewatered, i.e., the chlorinated hydrocarbons, specifically ECH and DCDIPE, both active carcinogens. Workers must wear protective gear (face masks with carbon filter cannisters and proper clothing/ gloves for skin protection) at all times. Secondly, as a precaution, it might prove wise for HAK-I to monitor the ambient air for total R-Cl. If the concentration is found to exceed safe limits (reference - Sax's Handbook on Industrial Chemicals - as a guide), it might be wise to provide the workplace with adequate ventilation (e.g., fans). Thirdly, the concept proposed to me that it may be possible to reuse the filter cake for agricultural soil stabilization strikes me as resourceful thinking. I would caution, however, that every effort be undertaken to insure that the residual chlorinated hydrocarbons will pose no future problems regarding plant uptake or transfer to vegetable crops.

5. Recommendations.

a. Because I am a firm believer in absolutely clean feedstocks, based upon my chemical engineering training and experience, together with what I have seen and evaluated here in Tuzla, I cannot unconsciously avoid the strongest recommendation that HAK-I management consider forsaking lime in lieu of caustic soda. Over 90% of your PO wastewater treatment difficulties (pre-treatment presently and municipal industrial combined biological treatment in the future) stem from the fact that the lime is of inferior quality. Caustic soda is produced within the factory limits, and the purity can be maintained. Although the cost of caustic soda is higher than lime initially, the benefits from its use have to outweigh the additional costs. The following table lists the Advantages versus the Disadvantages of choosing this recommended alternative:

NaOH

Disadvantages

(1) Higher cost of feedstock NaOH (but lower PO cost overall).

(2) Some equipment modifications: storage vessels, pumps, etc.

(3) Added safety precautions.

(4) Possibly some more PG produced in saponifier.

Advantages

(1) Can be used in a scrubber to wash unreacted propylene and propane in the propylene feedstock, which leave the top of the PCH reaction tower, to remove HCl and any residual Cl_2 and allow recycle or use elsewhere in the plant as fuel, e.g., incinerator feed make-up.

(2) Fewer side reactions in saponifier due to absence of R_2O_3 and MgO. Also longer impeller and diaphragm life in pumps due to absence of grit and sand from lime.

(3) Elimination of thickener-sedimentation unit now used to process solids in Wastewater Stream -3.

(4) Elimination of ash removal device and filter press and, therefore, no need for ultimate disposal of dewatered filter cake.

(5) Possible elimination of need for larger equalization vessel to replace mixing tank prior to steam stripper.

(6) Increase in efficiency of steam stripper (reduced scaling on packing material - no SiO_2 to deal with).

(7) Significantly reduced SS concentration.

(8) Wastewaters from process that are more consistent and equipment with fewer problems.

(9) Better cooling tower operation.

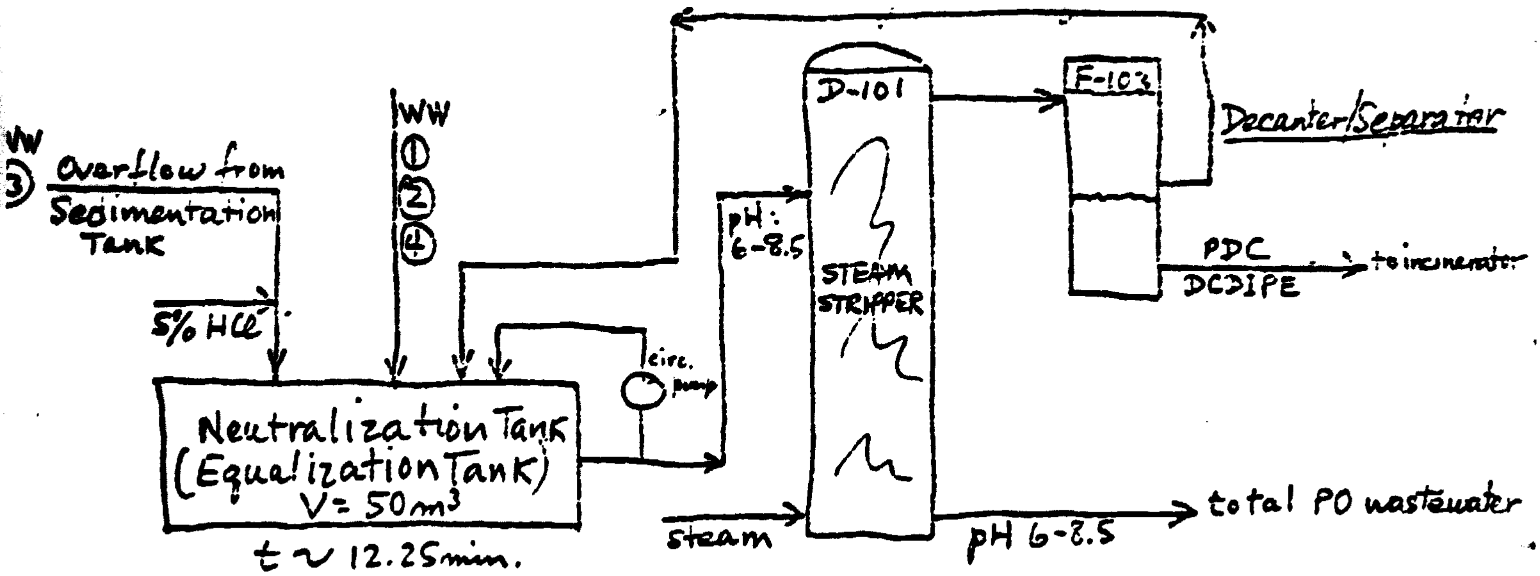
(10) Able now to take advantage of Dow Chemical Co.'s experience in treating of similar wastewaters biologically.

(11) Significantly reduced load on proposed biological system.

(12) In general, minimization and simplification of PO wastewater pretreatment.

(13) Reduction in frequency of monitoring requirements.

b. In lieu of the fact that the steam stripper is the heart of the PO plant's pretreatment system, I believe that it should be allowed to function as designed. Therefore, I proposed to substitute the neutralization vessel in place of the mixing tank as follows:



It is also possible to use the present mixing tank (F-101) for neutralization of clarified Wastewater Stream -3 prior to its passage to the equalization tank. There are two functions for the vessels as described here: (1) neutralization of Wastewater Stream -3, and (2) equalization of Wastewater Streams -1, -2, -3, -4 in order that fluctuations in concentrations may be dampened before introduction of the completely-mixed wastewater, at pH 6-8.5, to the steam stripper. In this way, the stripper may be allowed to operate as originally designed - as a unit operation for the separation of chlorinated or more volatile organics from water through the driving force of steam. No additional neutralization would be required after stripping and the treated wastewater may be discharged, without further cooling, to the combined industrial-municipal treatment plant.

Furthermore, I believe it would be sagacious to recommend that the previous pretreatment modification be pilot-plant evaluated at a scale sufficient to give statistically reliable data. Of prime concern are operational data to establish the optimum pH requirements or range for the stripping column. This should also reduce the HCl requirement somewhat.

c. You should be aware that only a properly designed and operated sedimentation tank, in advance of the neutralization and equalization vessels, can be tolerated. The inorganic precipitated solids and inerts can then be removed from the grit blow-off and drain and discarded to a landfill and the $Ca(OH)_2$ concentrated in a thickener for subsequent recycle as make-up to the saponification unit, as is common practice in the U.S. (This assumes that lime is still used, of course.)

d. I believe it advisable that a proper staff member from the Institute or HAK-I arrange a visit with Dr. Eberhardt Dyhrenfürth at the Dow Chemical Co. research facility in Horgen, Switzerland (near Zürich), if he is available. He is considered Dow's PO expert.

e. If it is still not possible to use caustic soda in lieu of lime, for either economic or political reasons or both, then I would recommend the following:

(1) Routine (composites from each new batch of lime) analysis of lime quality, particularly ash, and most importantly, to assess the activity of the CaO.

(2) Pre-treatment of lime to reduce:

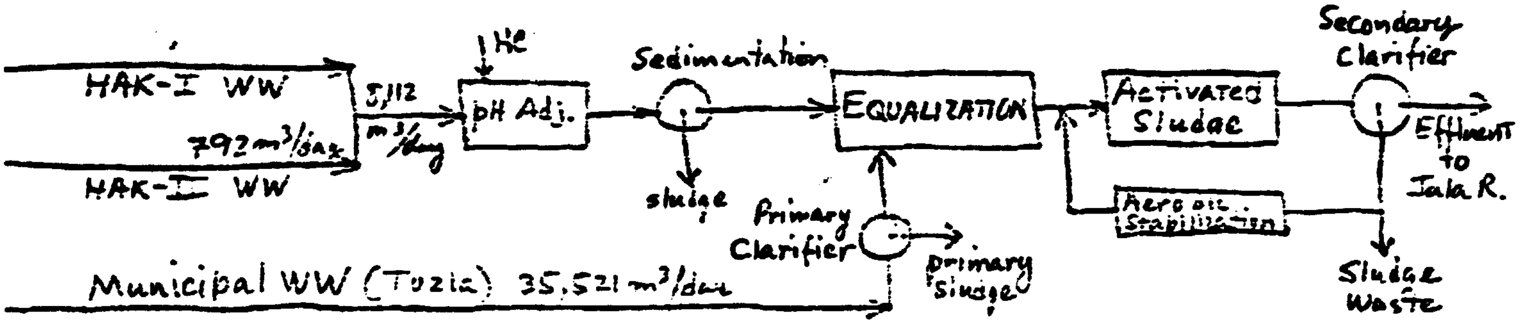
$MgO \leqslant 1.0\%$
$SiO_2 < 0.2\%$
$R_2O_3 < 1.0\%$
$SO_3^= < 1.0\%$
ash $< 1.0\%$

The final CaO active content should be >95% at all times. This pretreatment will result in the use of additional equipment and generate substantial quantities of sludge, >5% of total lime, which, of course, will have to be disposed of properly in an appropriate landfill. However, the extra expense will result in added savings relative to both PO quality and quantity and significantly reduce PO process pretreatment costs. These savings should more than offset the incrementally higher lime pretreatment expenditures.

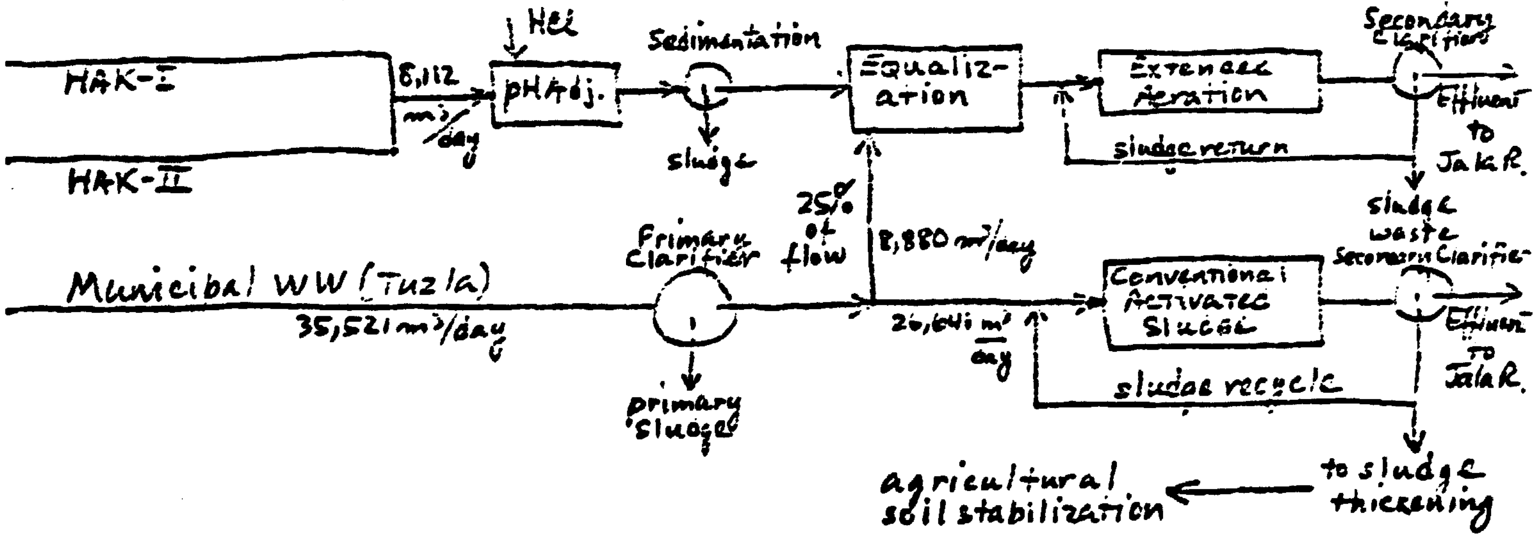
B. Municipal-Industrial Wastewater Treatment

1. HAK-I, HAK-II, and Municipal Wastewater Treatment Options.

a. Option 5.



b. Option 7.



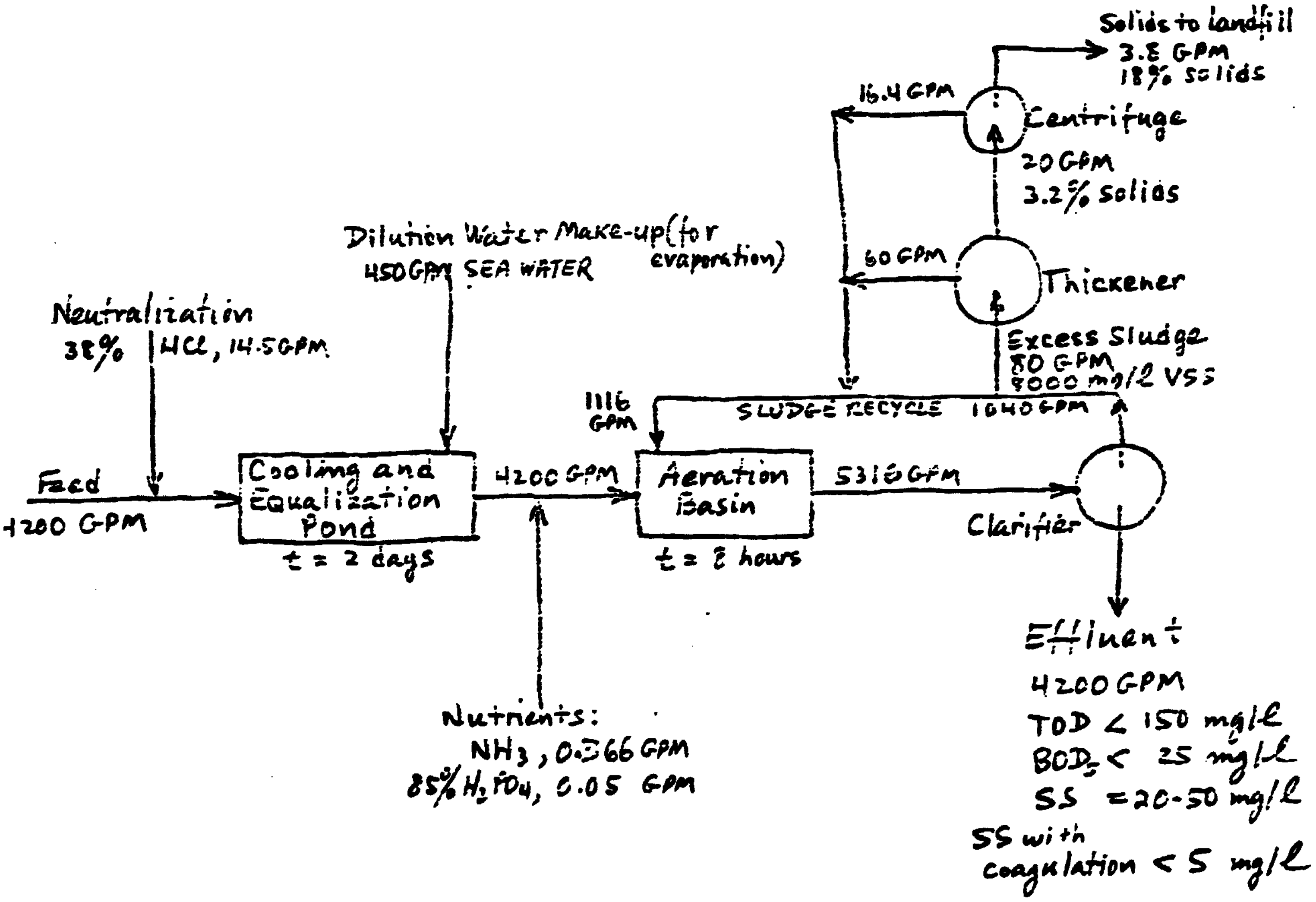
(A more detailed evaluation with recommendations is contained in the section titled: Recommendations.)

2. Comparison to Dow Chemical Co. Wastewater Treatment Scheme.

The following design specifications were used by the Dow Chemical Co., Freeport, Texas for a 6 MGD (22,700 m^3/day) activated sludge wastewater treatment plant:

Flow Rate	4200 GPM (15.75 m^3/min)
NaCl	9.0%
Specific Gravity, 20°C.	1.063
NaOH	0.18%
Temperature	180°F. (82.2°C.)
TOD	1400 mg/l
BOD_5	510 mg/l
Propylene Glycol	640 mg/l

A schematic of the treatment process follows:



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The major conclusion of the investigation was that the results obtained demonstrated that a significant advantage exists for the completely-mixed mode of operation especially if the feed is equalized to dampen the changes in organic chemical loading.

3. Discussion of Potential Problem Areas.

a. Suspended Solids Removal/pH Adjustment.

A properly maintained and operated wastewater treatment facility must, by definition, provide adequate pH adjustment and suspended solids removal prior to the wastewater undergoing equalization and subsequent biological and/or physical-chemical treatment. The reasons for this prerequisite are obvious. A truly biological system cannot function optimally in a pH range outside 7-8.5 or with a suspended solids load predominantly comprising inorganics, e.g., $Mg(OH)_2$, $MgCO_3$, $CaCO_3$, $CaSO_4$, $Ca(OH)_2$, SiO_2, etc. These inorganic constituents tend to cause less than satisfactory effects on the biomass resulting, on the one hand, in the generation of filamentous particles, or on the other hand, thin or finely-divided MLVSS that will have the tendency not to settle even under the most beneficial conditions.

b. Equalization Tank/Pond.

I cannot overemphasize the importance of this vital segment in the overall sequence of the treatment scheme. Good environmental/sanitary engineering practice dictates/mandates the utilization of such a device whose sole purpose is to dampen or even-out fluctuations in organic chemical loading emanating from HAK-I and HAK-II.

Normal design rule-of-thumb states that a minimum 2-day retention time be employed. However, in the case in question, I realize this to be impractical. Therefore, I propose that an 8,112 m^3/day x 2 days $\cong$ 16,000 m^3 reservoir be used. I cannot, in all honesty, envision a smaller-sized unit that would offer sufficient protection to the biology within the extended aeration basin, recalling that 8,112 m^3/day of HAK-I and HAK-II wastewater are to be combined with 8,880 m^3/day of municipal wastewater (25% of total wastewater flow or Option 7) - a minimum case condition. Recall that the advantage of the extended aeration concept is to allow the biota present therein additional oxygen for respiration to acclimate to the harsher conditions of stronger than normal industrial wastes. I believe that sacrificing retention time, i.e., volume, in the equalization tank, is removing that last measure of safety for the already overstressed biomass.

c. Pilot Plant Evaluation.

Prior to full-scale design and ultimate construction of a wastewater treatment facility, good engineering practice and common sense dictate that pilot plant studies and evaluation precede any major engineering decisions. Such pilot-scale evaluations should be representative of both concentrations of chemical wastes to be treated together with proportionally envisioned flowrates. Therefore, I believe it in the best interests of those in the decision-making process to contemplate a pilot plant scale in the range of 1,000 - 10,000 l/day. Such an investigation should also consider as mandatory the obtaining of the following design parameters:

(1) Removal efficiency for the parameter chosen, e.g., TOC, TOD, COD, BOD_5, etc.

(2) Optimum temperature for the activated sludge.

(3) Allowable temperature range of operation.

(4) Nutrient requirements,if any.

(5) [TOC, TOD, COD, BOD_5, etc.] removal rate.

(6) Oxygen utilization.

(7) Oxygen transfer (α and β).

(8) Sludge production.

(9) Optimum loading range, i.e., kg TOD/kg MLVSS-day.

(10) Bacterial species identification.

During the conduct of the pilot plant investigation, certain facts, obtained from previous studies, should be borne in mind:

- The presence of sustained high chlorides (Cl^-) generally depresses respiration, but periodic operation at low chloride concentration has been found to improve the tolerance of activated sludge to high chlorides.
- In the biochemical oxidation of propylene glycol, acetol appears to be the first oxidation product. This metabolite has been identified by GC-MS. Traces of acetic acid were also detected in some of the intermediate samples.

- Dilution of the propylene glycol wastewater (or propylene oxide, if you prefer it) to a salt (NaCl:recall caustic soda was used as the saponification agent) content of 6-8% appeared to increase the rate of TOD removal appreciably with the mixed culture used.

- Loadings below 1.5 lbs TOD/lb MLVSS-day resulted in a sudden loss of bacterial concentration, whereas at loadings over 4.0 or 5.0, filamentous bacterial growth resulted, with poor settling properties and a resultant high concentration of suspended solids in the effluent from the settling tank or clarifier. The recommended range of organic loading for this mixed (acclimated) culture is: 1.5-3.0 lbs TOD/lb MLVSS-day.

- The most numerous bacterium present is a gram-negative, non-motile, oxidase-positive rod. Biochemical tests reactions of 48 isolates from the activated sludge indicated that there were no more than three or four species.

- The growth of this culture is favored at higher temperatures. Good operation was maintained during the summer months at 100°F. (43.3°C.), but difficulties were encountered at temperatures below 55°F. (13.3°C.), during winter operating conditions. The temperature of the aeration basin was maintained at 95°F. (35°C.) by heating, as a result.

- The optimum oxygen uptake appeared to be at a temperature between 30-35°C.

- A lower ratio of active oxygen demand to endogenous respiration seems to be a characteristic of halophilic bacteria that differentiates it from freshwater bacteria (example: ratio of AOD/ER ~ 2 for halophilic versus ~ 5 or 6 for freshwater).

- Sludge settling experiments showed that with an initial bacterial concentration of >1,100 mg/l, 90% suspended solids removal could be obtained in about 20 minutes. Sludges with concentrations <1,000 mg/l took much longer to settle. During periods of disturbances in the plant operation, samples of the sludge had a sludge volume index (SVI) as high as 100, for which a removal of 70% required over 100 minutes. Under normal operating conditions, the SVI varied between 50-60, and 90% of the sludge settled in <20 minutes.

- The halophilic bacterial culture requires higher concentrations of nitrogen and lower concentrations of phosphorus than the freshwater cultures reported in the literature. A ratio of TOD:N:P of 300:10:1 was found to be the optimized value for the nutrient requirement. For an average of 1,500 mg/l TOD in the PO wastewater (BOD_5 = 540 mg/l), 50 mg/l NH_3-N and 5 mg/l PO_4-P fed gave a residual of 8 mg/l N and 1-2 mg/l P in the effluent.

- Results showed that a significant advantage exists for the completely-mixed mode of operation, particularly if the feed is equalized to dampen the changes in organic loading.

d. Polyol Wastewater Effects on Biological Treatment.

I have reviewed the following data regarding projected wastewater flows and characteristics for the polyols production within HAK-I:

Q avg : 1154 m^3/day
Q max : 1320 m^3/day
BOD_5 daily avg : 632 kg/day
COD daily avg : 1560 kg/day
Temp. daily avg : 19.5-32.7°C.
SS daily avg : 30 kg/day
pH max : 3.7-11.0
pH min : 3.5- 9.1
$SO_4^=$ avg : 88.4 kg/day

From these data and other figures made available to me, and assuming the selection of Option 7, I have constructed the following table:

Wastewater Source		Q max m^3/day	% of Industrial Total	% of Combined* Total
HAK-I	PO	5,880	72.5	34.6
	Detergents	120	1.5	0.7
	Polyols	1,320	16.3	7.8
HAK-II		792	9.8	4.7
	sub-total	8,112		47.7
Municipal (25% of total)		8,880	-	52.3
	Total	16,992		

* Combined Total = Industrial + 25% of Municipal (Option 7).

Hence, if one uses the 7.8% of combined wastewater flow to the equalization and extended aeration basins and applies it to the pollutant concentrations depicted in the upper table on this page, one arrives at the following figures, based on dilution alone (see p. 11 , B.1.b schematic):

Source of Wastewater	Q max m^3/day	% of Combined Total Flow	BOD_5* avg kg/day	COD* avg kg/day	SS* avg kg/day	$SO_4^=$* kg/day	Cl^-* kg/day	o-DCB * kg/day
PO	5,880	34.6	1103.	3,644.8	3,187.	345.7	32,351.	0
Detergents	120	0.7	0.2	0.6	-	-	-	0
Polyols	1,320	7.8	49.3	129.5	7.	6.9	50.5	0.57
HAK-II	792	4.7	10.7	32.0	4.6	40.1	-	-
Muncipal	8,880	52.3	-	-	-	-	-	-

* Estimated pollutant loads to combined (industrial + 25% of municipal) wastewater treatment plant (Option 7).

It therefore becomes apparent that the polyol wastewater with its content of organic and inorganic components does not account for a significant portion of the total load reaching the combined wastewater treatment facility, in any category denoted.

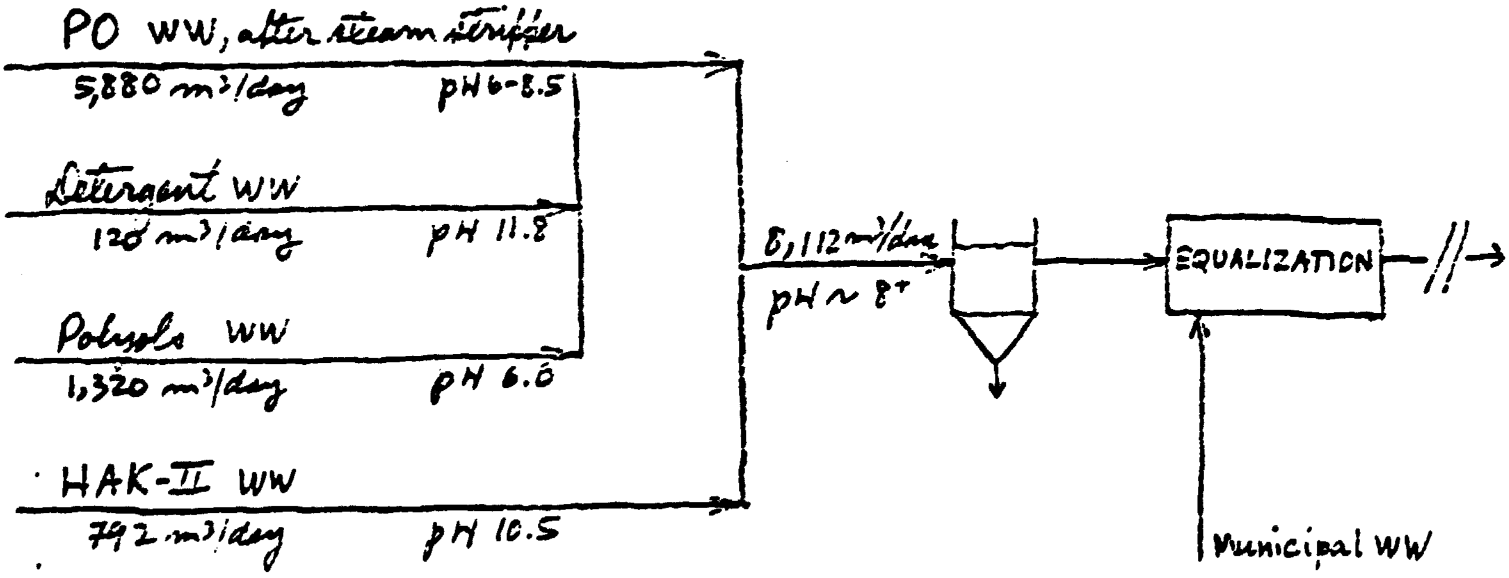
This estimated evidence, together with the hard evidence gathered by the Institute of Chemical Engineering regarding the susceptability of the polyol wastewater to biological treatment, lends credence to the conclusion that this wastewater should pose no real treatability problem. This conclusion requires only to be verified in the pilot plant studies.

e. Detergent Plant Wastewater Effects on Biological Treatment.

Referring to the calculations presented for this segment of HAK-I in the table on page 16a, there appears to be no reason to warrant any concern that this wastewater will cause problems to the biology in the aeration basin. However, one word of caution - it should first be established that no significant alkyl benzene sulfonate (ABS) compounds be discharged in the wastewater or they will play havoc with the operation of the biological treatment system due to their respective foaming potential.

f. HAK-II Wastewater Effects on Biological Treatment.

Careful examination of the calculations shown in the table on page 16a will show that the HAK-II wastewater flow only represents 4.7% of the total influent flow to the treatment system outlined on page (Option 7). Therefore, organic loading does not appear to present any major problems. What may prove to be the major concern with HAK-II wastewater, however, are the relatively high concentrations of $CO_3^{=}$. I believe these to be controllable in any regard and I propose that the following scheme be investigated in order that the HCl requirements be evaluated with due regard paid to analysis of any significant reduction in inorganics as a result of this treatment.



Residual $SO_4^=$ may cause scaling problems, but recall that $CaSO_4$ has an inverse solubility with increasing temperature. Conditions of higher temperature and co-precipitation with other insolubles may create a synergistic, positive effect.

The final significant item that must be regarded highly is the presence of o-dichlorobenzene used as a solvent in HAK-II. After dilution it accounts for only 0.57 kg/day load. Now, whether its presence is controlling or not depends entirely on how well acclimated the microorganisms are. They will prefer as food, I believe, aliphatic organics, but quite possibly there will develop sufficient quantities of o-DCB-loving microorganisms within the active biomass. Again, pilot plant investigations will prove immensely important in this regard.

g. Carbon Adsorption as a Potential Tertiary Step to Attain the Water Quality Requirements.

If the selected combined industrial-municipal biological treatment system is unable to meet the Water Quality Requirements of 20 mg/l BOD_5 and 30 mg/l SS and the recommended limits for specific chlorinated hydrocarbon compounds, specifically o-DCB, ECH, and DCDIPE, then I believe it wise to consider the potential of employing a tertiary carbon adsorption system to "polish" the effluent. Certain information, obtained by Dow Chemical Co. and the Calgon Corporation are therefore summarized below.

- o The high adsorption capacities of activated carbons may be useful in removing low concentrations of chlorinated hydrocarbons that might be toxic, as a pretreatment step, prior to the activated sludge process, provided that the specific stream can be isolated and so treated, so as to minimize the carbon requirements.

- o The capacity of carbon for PG and the like from wastewater feed is about half of its capacity when a synthetic solution is fed under normal operating conditions. This is partly due to the competitive adsorption of the chlorinated organics in the waste stream.

- o The capacity of activated carbon for ECH and DCDIPE is very high compared to the glycols.

- o The uptake of glycol increases with increasing pH. An increase in pH quite probably results in an increase of the negative charges at the surface of the carbon, thus enhancing the adsorption of the positively-charged glycols that are known to be hydrogen-bonded with the water molecules.

h. Shot Pond.

One should never forget that there are always emergency situations that occur within a chemical manufacturing complex. A batch of polyol may be required to be purged suddenly from a reactor or an unexpected impurity in the PCH reactor may produce a higher than normal concentration of PDC, whereupon the entire reactor's contents have to be purged immediately to maintain safety. What then? Provision must be made for a "shot pond" or emergency receptacle for such a discharge, more than likely located within the confines of HAK-I or HAK-II or both.

4. Recommendations.

a. First and foremost among my recommendations is the dire need for an adequate equalization pond of proper size whose design incorporates the best engineering judgment. I firmly believe that the decision makers would be ill-advised to accept an equalization pond with less than a 16,000 m^3 volume for the reasons contained in the discussion on page 13 .

Furthermore, I strongly advise that a small, biological reactor, which is capable of simulation of what actually is occurring within the aeration basin, be developed. Such a biological reactor would be designed to monitor dynamically and spontaneously if a particular trace organic chemical is capable of producing a toxic effect on the biomass, before it actually occurs in the normal operating scheme. Laboratory investigations, therefore, should commence well in advance of the actual start-up of the full-scale treatment facility.

b. The same can be said of the need to initiate pilot plant investigations of the treatment sequence well before final specifications for the treatment plant are put out to bid. The pilot plant should be scaled in the range of 1,000-10,000 l/day. Specific details of what design parameters are to be considered are presented on page 14 of this report.

c. I recommend that the pH adjustment scheme shown on page 17 be thoroughly investigated to ascertain its merit.

d. I have studied in detail the two most reasonable alternative industrial-municipal wastewater treatment combinations that are depicted on page 11 and have considered also the economic feasibility of each. I certainly endorse their selection from among the seven alternatives presented. I have come to the conclusion that, in my professional opinion, that Option 7, although slightly more costly in capital and operating costs, is the more flexible of the two and is well worth the additional outlay of funds. My reasons for this decision are mainly twofold: firstly, the utilization of extended aeration is well suited to an industrial wastewater with the complexity of that with which we are dealing. With future growth and expansion in the HAK-I and HAK-II complexes a predictable occurence, Option 7 possesses the flexibility required by such a forward moving industry as that dealing with petrochemical manufacturing.

Option 5, in the meantime, has little flexibility built into the design and would require a humungous equalization basin and does not include provision for reuse of biologically produced sludge. Besides, the sludge generated would contain unknown amounts of toxic chlorinated hydrocarbons both passing through the activated sludge untreated because of their refractory nature and unknown and potentially more toxic metabolites, whose presence within the spent sludge would preclude its proper utilization as an agricultural soil stabilizer, and requiring an extremely large dewatering system and ultimate disposal landfill site. Furthermore, the presence of the potentially toxic organics and metabolites quite possibly would lead to pollution of the groundwater resources located beneath the landfill site chosen.

Option 7, however, allows reuse of that portion of the sludge generated from the municipal wastewater (75% of total flow) treated in the conventional activated sludge process. Such a sludge has known characteristics and may be used as an agricultural soil stabilizer, thus resulting in a sizable return on the original investment costs.

I believe Option 7 to be a well thought out alternative worthy of the full support of the decision makers.

e. My final recommendation deals with what I feel would be most beneficial to the team of scientists and engineers working at the Institute. Because the wastewaters produced at HAK-I and HAK-II are rather unique, they require specialized and advanced treatment methods, not normally well known or understood. I feel it is in the best interests of all parties, that a staff member contact Dr. Willard Taber, Professor of Biology at the Texas A&M University in College Station, Texas to further his/her education and experience in the biology of halophilic bacteria. Dr. Taber is one of the few people in the world who has spent the last 10 years investigating this subject.