REFERENCE 9

PROGRESS REPORT
ORGANIC CHEMICALS DIVISION
TECHNOLOGY DEPARTMENT

Aroclor

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PROJECT TITLE

Dept. 246 Aroclors. PCB Removal from HCl Off Gas.

PROJECT OBJECTIVE

Develop a process that will permit reduction of all chlorobiphenyls (mono-poly) in the HCl off-gas from the Aroclor Department such that when all the gas is sewered the total chlorobiphenyl content will be less than 2.5 lb/day. Zero lb/day would be preferred.

Summary

Both 1016 bottoms and chlorosulfonic acid have been found to be effective scrubbing liquids for the removal of biphenyl and chlorobiphenyls from Dept. 246 (Aroclors) off-gas HCl. By employing a 10 or 15-tray Oldershaw column and scrubbing HCl gas containing biphenyl and chlorobiphenyls at levels equivalent to the off gas from production units the total detectable polychlorobiphenyl (PCB) found was well below the level required to meet the project objective.

Of the two scrubbing liquids, the chlorosulfonic acid affords us a lower PCB level in the scrubbed gas. However, this potential benefit is offset by the high cost of equipment and disposal problem associated with the used C/S acid. The use of 1016 bottoms on the other hand will require less expensive equipment, is compatible with the Aroclor process and could provide an opportunity for some yield improvement. No disposal problems are anticipated because the used 1016 scrubber can be further chlorinated to make Aroclor 1254 or 1260.

With appropriate carbon treatment, industrial grade muriatic acid made with this scrubbed gas should meet the proposed PCB limit of 10 ppb.

Summary (Cont'd)

Engineering data required to design a suitable scrubbing system using either C/S acid or 1016 bottoms was also generated during this study and is communicated in the details section.

II. Recommendation

One practical way it appears of reducing the chlorobiphenyl content in HCl off-gas to meet environmental pollution standards and also provide an HCl feed source for the adiabatic absorber is to scrub the gas with either chlorosulfonic acid or 1016 bottoms. It is recommended therefore, that a scrubbing system be designed and installed using one of these two materials as the scrubbing liquid.

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III. Details

A. Introduction

The HCl off-gas from Department 246 (Aroclors) presently contains significant amounts of biphenyl, monochlorobiphenyls and polychlorobiphenyls (PCB). Calculation and laboratory analyses of sewer samples indicate that if all the by-product HCl were sewered the total PCB losses could be 15-30 lbs/day. Because of recent unfavorable reports on the negative ecological effects of PCB's and also from the standpoint of waste water treatment here at the Plant it is a must to reduce the PCB losses to less than 2.5 lb/day. Zero lb/day are preferred.

At the same time, however, it is important that whichever approach is undertaken to remove the PCB's the following factors be given primary consideration:

a. The process must permit the reduction of PCB in the HCl gas to extremely low levels, <40 ppm.

b. The process must be compatible with Dept. 217 process and the finished goods, chlorosulfonic acid.

c. Scrubbed HCl gas be suitable as a feed source for the adiabatic absorber to produce industrial grade muriatic acid.

In this study we plan to take advantage of the extremely low vapor pressures of the PCB's and thereby remove them from the gas stream by some kind of scrubbing system.

B. Experimental Work

1. HCl gas Scrubbing Setup and Procedure

A diagramatic sketch of the experimental gas scrubbing system is shown in Figure 1. Scrubbing experiments were carried out using 5, 10 and 15-tray Oldershaw columns. Hydrogen Chloride (HCl) gas was saturated with biphenyl and chlorinated biphenyls by scrubbing with MCS 1109 and off gas condensate at 50-60°C and 45-50°C respectively. The composition of these two scrubbing liquids are shown below:

	MCS 1109	Off-Gas Condensate
Biø	22.24%	24.74%
O-CBP	58.60%	22.63%
M-CBP	4.03%	7.29%
P-CBP	14.66%	11.62%
Di-CBP/HiB	0.47%	33.72%

Experimental Work (Cont'd)

The composition of the organics in the gas scrubbed through MCS 1109 averages about 400 ppm biphenyl, 650 ppm monochlorobiphenyl and <1 ppm polychlorobiphenyl (PCB). HCl scrubbed with off-gas condensate contains about 250 ppm biphenyl, 107 ppm monochlorobiphenyl and 150 ppm PCB. This composition compares with the typical plant off gas HCl that is sent to Dept. 217 for C/S acid production or to the sewer. Gas feed rate varied between 500-600 cc/min. (1.1 SC FH) and liquid flow from 10-12 cc/min. (1.2-1.5 lb/hr.).

The saturated HCl gas was fed to the bottom section of the scrubbing column. The scrubbing liquid was fed to the top of the column. In some experiments the liquid effluent from the column bottom was recycled to the process. The feed gas stream to the scrubbing column and the outlet gas from the column were analyzed for biphenyl, monochlorobiphenyls and polychlorobiphenyl (PCB) content by scrubbing a known weight of the HCl gas with hexane. Sampling was done by first scrubbing the HCl gas with hexane and then through an aqueous solution containing exactly 1 Mole of sodium hydroxide and phenolphthalein indicator. When the caustic scrubber changed from red to colorless the sampling was stopped. All the sample lines were heated to prevent any possible loss of PCB due to condensation or entrainment.

2. Analytical Methods

The biphenyl and monochlorobiphenyl content in the HCl gas were measured by a flame ionization detector GLC. An internal marker was added to the hexane scrubbed sample, which was then filtered through dry sodium sulfate and condensed to about 5 ml. This particular method is only accurate for biphenyl and monochlorobiphenyls only. The polychlorobiphenyl (PCB) content in the HCl was measured by an electron capture (E.C.) GLC. This method does not measure the biphenyl or monochlorobiphenyl content. It is therefore necessary to use both methods to determine the composition of the impurities in the HCl off gas samples. It should also be pointed out, that the present PCB method does not differentiate the various isomers, but merely indicates whether Aroclor 1221, 1242, 1248, 1254 or 1260 is present.

Absolute precision and accuracy of the analytical methods used was not determined for this application. The results are judged to be adequate for the purpose of the design of the scrubbing equipment. Information concerning determining accuracy under these conditions will be obtained before design is complete.

C. Experimental Results and Discussion

1. Screening of Scrubbing Liquids

Several possible scrubbing liquids were evaluated. These were selected primarily on the basis of being relatively cheap, available, good solubility for chlorobiphenyls, low pour points, low vapor pressure and compatible with Dept. 217 process and the finished chlorosulfonic acid. Table 1 lists some of the various scrubbing materials tested using a 5-tray Oldershaw scrubbing column.

Table 1

Scrubbing Liquid	Result
Oxo-alcohol bottoms	Not effective
HB-40	Effective
Aroclor 1242	Effective
Aroclor 1242 & 1254	Effective
1016 Bottoms	Very effective
Chlorosulfonic Acid	Very effective

On the basis of the results from these initial screening runs it was felt that 1016 bottoms and chlorosulfonic acid had the most to offer, meeting two or more of the criterions specified. A more detailed study involving these two liquids were then undertaken.

2. Chlorosulfonic Acid Scrubber

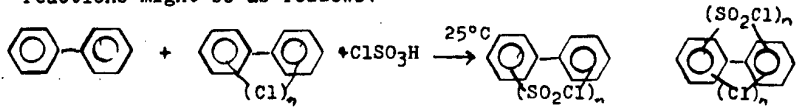
Several runs were made with chlorosulfonic acid using 5, 10 and 15-tray Oldershaw columns at 25°C. In some cases the chlorosulfonic acid was passed once through the column while it was recycled in others. Complete results of scrubbing study with chlorosulfonic acid are shown in Table II. The experimental data indicates that the 5-tray column with no C/S acid recycle will essentially remove all the biphenyl and monochlorobiphenyls and about 90% of the polychlorobiphenyls. The use of 10 and 15-tray columns were even more efficient, with the scrubbed gas having less than 1 ppm PCB.

It appears that no additional benefits are obtained by going from a 10 tray to 15 tray column.

When the chlorosulfonic acid was recycled to the process there was a slight increase in the PCB level in the scrubbed gas. Recycling had no effect on the biphenyl or monochlorobiphenyl, which were still less than 0.1 ppm. These results indicate that it is feasible by using a chlorosulfonic acid scrubber the PCB level in Aroclor HCl off gas can be reduced to less than 1 ppm. Figure II shows GLC chromatograms of feed gas before and after scrubbing with C/S acid using 5, 10 and 15-tray Oldershaw columns.

Experimental Results and Discussion (Cont'd)

It is suspected that the chlorosulfonic acid is acting more than just a physical scrubbing system and is actually chemically reacting with the biphenyl and chlorobiphenyls to form solid sulfonyl chlorides which remain the liquid C/S acid. Typical reactions might be as follows:



Although the use of chlorosulfonic acid did an excellent job in reducing the PCB's there are a number of problems associated with its use. These are listed below:

1. Expensive equipment.
2. Disposal of used scrubber liquid.
3. Safety of personnel.
4. System would have to be completely anhydrous, because of the violet hydrolysis of C/S acid with water.

3. 1016 Bottoms Scrubber

The use of 1016 Bottoms is probably the most logical choice for a scrubbing liquid. This material consists mainly of tri, tetra and penta-chlorobiphenyls. It is quite viscous at room temperature, but is a easy flowing liquid at 40-45°C. 1016 bottoms are also compatible with organics being removed from the off gas and with the Dept. 217 process and finished goods C/S acid. HCl gas saturated with off gas condensate was scrubbed with 1016 bottoms at 40-45°C using 5, 10 and 15-tray Oldershaw column. Results of this series of experiments are shown in Tables III and IV and Figure III.

Temperature has a very important effect on the operating efficiency of the 1016 bottoms scrubber. The temperature must be high enough to allow easy flow of the normally heavy and viscous 1016 bottoms, but not too high as to significantly affect the vapor pressure of the contaminants being removed. The results in Table III show the significant increase in biphenyl and monochlorobiphenyl content in going from 42-80°C. Care should also be exercised to maintain the temperature about 40°C to keep the 1016 bottoms from possible solidifying. Laboratory work indicated that 40-45°C was the preferred temperature to operate the scrubbing column.

Experimental Results and Discussion (Cont'd)

The laboratory study also showed that the removal efficiency of biphenyl and monochlorobiphenyl increases with the number of trays employed in the scrubbing column. The 5-tray column removes about 95% of the biphenyl and about 80% of the monochlorobiphenyls. Better than 99% of these contaminants are removed by the 10-tray column and there is essentially a 100% removal with a 15-tray column. However, with regards to the removal of the polychlorobiphenyls (PCB) the 5-tray column appears just as efficient as the 15-tray column. The saturated HCl with an initial concentration of 137 ppm PCB averages about 9 ppm PCB, after scrubbing and this value compares favorably with the calculated value of 11-18 ppm PCB for pure HCl saturated with 1016 bottoms. If the Plant HCl off gas can be lowered to about 9 ppm PCB and all this gas were sewered the total daily loss would be about 1 lb. versus the present 15-30 lbs.

It was observed that the 1016 bottoms used in the scrubbing experiments had a tendency to solidfy to a white mass at room temperature, while the unused portion still remained a clear heavy liquid. This white mass melted at about 26-30°C to give the normal clear liquid. The unused 1016 bottoms also solidified on standing at room temperature when seeded with particles from the solid HCl scrubbed bottoms. This problem can be eliminated in plant operations by keeping all piping and storage facilities above 40°C.

IV. References

OR Notebook Pages 192346-192359.

WGK Notebook Pages 17501-17515.

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Figure I - Schematic Diagram of Laboratory Scrubbing System

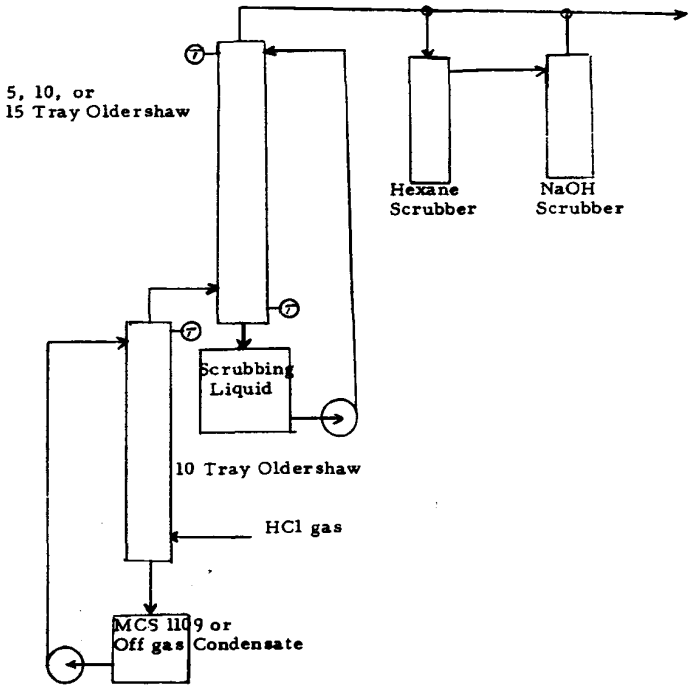

Figure 3 - HCl Scrubbed with 1016 Bottoms
(Feed stream similar to Run 17 in Figure 2)

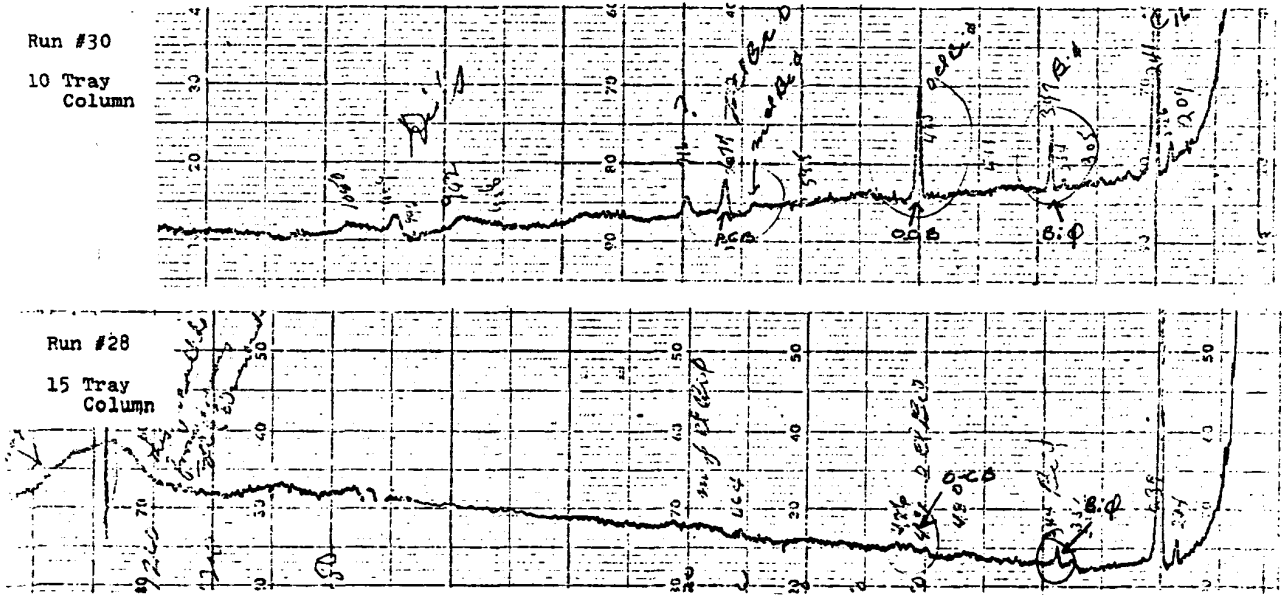

Table IV. Aroclor HCl Off Gas Scrubbing Data
1. Effect of Tray Efficiency
2. 1016 Bottoms Scrubbing Liquid
3. Scrubber Temperature 40–45°C

Run No.	No. of Trays	Inlet HCl Gas (ppm)							Outlet HCl Gas (ppm)							Comments
		P.I.Analysis			P.C.Analysis				P.I.Analysis			P.C.Analysis				
		B1Ø	MCB1Ø	PCB	1221	1242	1254	PCB Total	B1Ø	MCB1Ø	PCB	1221	1242	1254	PCB Total	
1	–	441	653	<1	–	–	–	–								HCl Scrubbed with MCS 1109
6	–	–	–	–	94	32	11	137								HCl Scrubbed with Off Gas Condensate
7	–	258	107		–	–	–	–								" "
1	5	411	653	<1	–	–	–	–	2	–	–	–	5	2	7	1016 Bottoms once through Column
1	5	"	"	"	–	–	–	–	20	57	<1	–	–	–	–	" "
1	5	"	"	"	–	–	–	–	13	26	<1	–	–	–	–	" "
4	5	258	107	–	94	32	11	137	–	–	–	–	4	7	11	" "
5	5	"	"	–	"	"	"	"	8	22	–	–	–	–	–	" "
9	10	"	"	–	"	"	"	"	–	–	–	None	None	8	8	" "
0	10	"	"	–	"	"	"	"	0.2	0.8	–	–	–	–	–	" "
1	10	"	"	–	"	"	"	"	–	–	–	None	None	11	11	Recycle 1016 (98 g HCl → 590 g 1016)
3*	10	"	"	–	"	"	"	"	–	–	–	None	None	34	34	" " (253 g HCl → 590 g 1016)
4	10	"	"	–	"	"	"	"	0.7	3	–	–	–	–	8	" " (300 g HCl → 590 g 1016)
7	15	"	"	–	"	"	"	"	<.1	<.1	–	None	None	2	2	1016 Bottoms once through Column
8	15	"	"	–	"	"	"	"	<.1	<.1	–	None	None	6	6	Recycle 1016 (126 g HCl → 480 g 1016)

I believe this sample was contaminated