Prod Res Activities January 1971

Carbon Adsorption Studies (IRansaw, Anniston)

The pilot study was terminated 1/6/71 without the indication of a breakthrough at average flow rate of 6 gpm/ft^2.

Presently, the data is being compiled for evaluation by the Calgon Division of Pittsburgh Carbon. Calgon will utilize the data to give the following information: a. design parameters, b. operational costs, c. capital investment.

Filtration Studies (IRansaw, Anniston)

The issuance of the R&D report covering this study was delayed. This report will now be issued 1/15/71.

Solid-Aroclor Removal by Flocculation (IRansaw, Anniston)

The installation of the clarification unit is progressing according to schedule. Start-up is targeted for 2/2/71.

The flocculation jar tests conducted on the plant effluent (by Betz Laboratorics) indicate that the best settling floc is obtained with 15 ppm of bentonite clay and 1.5 ppm of their polyelectrolyte 1170 additives. These results were demonstrated at the Anniston site by a Betz representative. Plans are now to use the flocculating agents recommended by Betz in the pilot tests.

The issuance of the work plan covering the flocculation study and the semi-continuous adsorption study will be issued 1/15/71.

Pollution Abatement, PR&D-Anniston (IRansaw/JLBrown)

BACKGROUND: The filtration and column adsorption phases of the work plan issued 9/9/70 have been completed. A report on the filtration study will be issued by 1/15/71. The data generated in the column study is being compiled for a cost estimate.

The following conclusions were drawn from the filtration study:

a. Aroclor levels of the plant effluent were reduced to 10 ppb by filtration of the neutralization pit solids on which Aroclor was adsorbed and by adsorption on the filtering media.

b. The removal of 200-1000 ppm of solids in the plant effluent is a primary concern in any final clean up system.

The line of research proposed in this work plan is based primarily on these conclusions. In the flocculation jar test run on the plant effluent, 15 ppm of SPV bentonite clay[1] and 1.5 ppm of Betz's 1170 polyelectrolyte gave the best settling floc.

Experimental: I. Define the following parameters in a flocculation study on the plant effluent.

a. Flow rate
b. Height of sludge blanket
c. Bentonite clay feed

Object: To determine the operational parameters at which the solid and Aroclor concentrations are reduced to a minimum (i.e. 0-20 ppm solids & 10 ppb Aroclors). Since the bentonite clay is only a weighting agent for the floc, its concentration will be increased to some practical limit if necessary, in order to provide more surface area for adsorption.

Estimated Beginning Date:	2/1/71
Mandays	40
Target Completion Date:	4/1/71

Experimental II. Demonstrate Aroclor removal in a semi-continuous adsorption study. Define optimum conditions:

a. Retention time
b. Adsorbent loading capacity
c. Recycle

Object: To utilize some less expensive adsorbents than carbon and provide an alternate design. The same reactor clarifier (Part I) will be used in this study. Provision will be made to recycle the settled adsorbent to premix area.

Mandays	40
Target Completion Date:	5/28/71

SAFETY: The HCl and H_3PO_4 in the plant effluent are normally neutralized in the limestone pit. Occasionally, there is some residual acidity which should be guarded against. Any area exposed to the waste water should be washed thoroughly with copious amounts of water. This will also remove any Aroclor present.

The flocculating agents (Betz polymer 1170 and American Colloid's SPV bentonite clay) are neither flammable, corrosive, or toxic. Hence, their handling requires no particular precautionary measures.

An operation manual containing all safety procedures will be issued to personnel operating the clarification unit.

(1) Product of American Colloid Company

MONS 033863

RESEARCH AND DEVELOPMENT REPORT
ANNISTON PLANT

Report No. 1
Job No. 446-514
Date January 15, 1971

OTHER LOCATIONS	GENERAL OFFICE	ANNISTON PLANT
	P. B. Hodges F. J. Holzapfel W. B. Papageorge W. R. Richard J. R. Savage	J. T. Bell J. L. Etheredge V. R. Haupt J. C. Landwehr G. W. Miller W. F. Taffee E. G. Wright

Title: Aroclor Pollution Study

Personnel: I. Ransaw & A. Nelson (J. L. Brown)

Problem: Removal of Aroclor from the waste water by filtration-adsorption.

Justification: Pollution Control

Summary: Aroclor was removed from the plant effluent by filtration of the neutralisation pit solids on which Aroclor was adsorbed and by adsorption on the filtration media. Aroclor concentrations (100-8,000) in the plant effluent were consistently reduced to 10 ppb upon passing through a four (4) inch diameter tube (packed to a bed depth of 5.5 inch with activated carbon) at flow rates up to 350 cc/min. In the sand filtration study conducted under similar operating conditions, the Aroclor levels in the effluent were not consistently reduced to the target level (< 10 ppb).

The presence of 200-1000 ppm of solid particles (size range 1.5-250μ) tended to blind the filter, thus setting a maximum limit on the pressure and flow at which the unit had to be operated.

Ish Ransaw
PR&D Chemist

jw

MONS 033864

BACKGROUND:

Initial Research efforts for removing Aroclor from the waste stream were centered primarily around three conventional approaches: multiple distillation, adsorption and extraction. After considering the economic and technical factors involved in each approach, it was felt the approaches should be evaluated in sequence listed above. The following paragraphs are presented to up-date previously research efforts and to show the basis for the work being reported.

Cost evaluations were made by Dr. Wise, CED, for both a distillation and extraction system for removing Aroclor from the waste water. Dr. Wise concluded that the cost for either of these systems was likely to be considerable greater than that for an adsorption system. A decision was made at this point to abandon these approaches and pursue the adsorption approach in depth.

Initial screening of various adsorbents (i.e, carbon types, porocal, attapulgus clay, powdered polyethylene) by adsorption isotherm tests was very inconclusive. The Aroclor levels were reduced to < 10 ppb in all the isotherm tests regardless of the adsorbent or the amount of adsorbent used. The reason for the erroneous results was later found to lie in the fact that Aroclor was being adsorbed on the reactor walls, particulates in the solution, as well as the adsorbent being tested. From the isotherm studies, the following conclusions were drawn: a) Aroclor levels in plant effluent can be reduced to an acceptable level (< 10 ppb) by adsorption. b) Further evaluation should be done on an adsorption column utilizing a feed of constant Aroclor concentration.

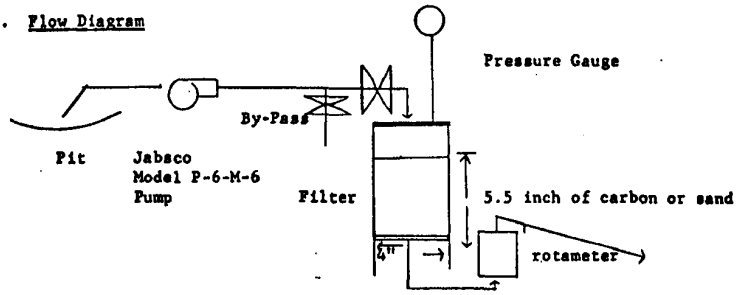
The studies reported herein were conducted at the original neutralization pit (hereafter designated as pit #1) and newly constructed neutralization (hereafter designated pit #2). Pit #1 was distinguished from pit #2, during the course of study, by both its consistently higher suspended solids and Aroclor concentrations. Pit #1 has been operational since 1961 while pit #2 has been operational since October, 1970.

In a 13 day pilot run at pit #1, initial concentrations of 1,000-8,000 ppb Aroclor in the waste were reduced to a range of 0-15 ppb upon passing through a series of packed carbon beds at a average flow of 25 cc/min. Over 99% of Aroclor removal occurred in the prefilter. This unusual reduction was found to be due, in part, to the filtration of solids on which Aroclor was adsorbed. Since the average flow per square foot was quite low for this particular study, it was felt that the prefilter observation should be evaluated at higher flow rates. This report contains the result of the studies carried out using both carbon and sand filtering media for treating waste water from pit #1 and #2.

1. The adsorber consisted of a prefilter (3.5 inch diameter packed to a 5.5 inch bed depth and a series of one (1) inch diameter columns packed to a total bed depth of 13.5 ft.

EXPERIMENTAL

1. Flow Diagram



*A 3.5 inch diameter tube was used in the carbon study at the old neutralization pit.

2. Sampling

A 24 hour composite sample (300 ml) was taken by catching a 100 ml. sample every 8 hours. Occasionally, smaller samples were caught at shorter intervals and composited.

3. Flow Rate

Flow to the filter was controlled by adjusting two needle valves (diagram above). A calibrated rotameter was used to measure flow. A given flow rate was difficult to maintain due to the back pressure created by the build up of fine solids in the filter. The unit was back washed when necessary to maintain a relative constant flow. In the studies conducted at pit #1, flows were started at the lowest rate (100 cc/min.) and then increased to maximum 350 cc/min. This approach was reversed in the sand study at the pit #2. The maximum flow (350 cc/min.) could not be maintained over an eight (8) hour period due to the high back pressure.

4. Analytical Analysis

The Aroclor was extracted from the aqueous sample into a hexane solvent. The hexane solution was then dried and analyzed on a EC/GC. The concentration of Aroclor 1221, 1242, 1254 was determined by comparing the main peak height of the unknown with height of the same peak in the chromatograms of known Aroclor solutions of 1221, 1242, and 1254.

DISCUSSION OF RESULTS

For clarity of the following discussion, it is necessary here to explain the difference in the quality of the effluent from pits #1 and #2.

During the course of this study, the effluent from pit #1 generally contained about 1,000 ppm of solids and Aroclor concentrations in the range (1000-80000 ppb) Table 1 & 2. A prolonged study of the effluent quality (i.e. solids and Aroclor levels) indicates that high Aroclor concentrations generally correspond to high solids. Presently, the solids level in pit #2 is kept at minimum. The effluent from pit #2 normally contains about 200 ppb of solids and 50-100 ppb Aroclor except during periods in which large quantities of acid (HCl) are being sewered. This accounts for the higher values seen in Tables 3 & 4.

Carbon consistently reduced the solid and Aroclor concentrations in the effluents from pits #1 & 2 to an acceptable level (< 10 ppb) at flow rates up to 350 cc/min. (Table 1 & 3). The mechanism by which Aroclor is being removed cannot totally be explained. Existing evidence indicates adsorption on the pit solids. However, attempts to determine the adsorptive capacity of the solids were unsuccessful. The lower quantity of solids (200 ppm) in the effluent from the pit #2 had seemingly little effect on the quality of effluent produced.

As it can be seen from Tables 2 & 4, the quality of effluent realized in the sand filtration was not as dramatic as in the carbon study. Aroclor levels in pit #1 effluent (Table 2) were significantly and rather consistently reduced without producing an acceptable effluent (< 10 ppb) quality. Comparatively, the effluent quality produced at the pit #2 was very inconsistent (Table 4). The effluent quality varied between high and low values without drastic changes in influent Aroclor levels or operating conditions.

The following factors may explain the results obtained:

a. The solids level of influent varied considerably during the test period.
b. Silica type adsorbent requires a considerably longer contact time to adsorb Aroclor than carbon.

The test data for both the sand and carbon studies suggest that the Aroclor removal is taking place by filtration of pit solids on which Aroclor has been adsorbed and by adsorption on the filtering media itself. Further, it also suggests that the adsorption zone with carbon is quite short and quite long with sand.

The solids in the waste stream caused considerable operational difficulties. These solids, of which 42% of its particles were in the 1.5 - 2.3 μ size, tended to blend the filter, especially at flow rates > 200 cc/min. Backwashing the filter did not adequately remove the finer particles. Hence, these Aroclor containing particles were eventually washed through the filter. This point was considered a breakthrough.

CONCLUSION

1. Aroclor is removed from the plant effluent by the filtration of the solids on which Aroclor was adsorbed.

2. Aroclor is adsorbed on activated carbon within a very short adsorption zone.

3. The effectiveness of sand in removing Aroclor is not sufficient at the experimental bed depth.

4. Solids removal is a primary concern in any final clean up method.

FUTURE WORK

1. A pilot adsorption study has been conducted in a series of 5 inch diameter columns. These result are being compiled for an evaluation and recommendation. A report will be issued by 1/28/71.

2. A pilot clarification (flocculation) unit is scheduled to be put in operation by 1/29/71. This unit will also be used to carry out semi-continuous adsorption studies with other finely divided solids.

Ishmeal Ransaw

jw
Attachments

CARBON FILTRATION STUDY AT OLD PIT

TABLE 1

Volume Treated (Gal.)	Aroclor Concentration of Influent (ppb) 1221	1242	1254	Average Daily Flow (GPM)	Aroclor Concentration of Effluent (ppb) 1221	1242	1254
38	84	106	NDA	0.0263	NDA	NDA	NDA
99	1750	188	NDA	0.042	21	14	NDA
160	NDA	618	NDA	0.042	NDA	NDA	NDA
*175	6051	2638	NDA	0.0263	7	5	NDA
198	559	147	NDA	0.0263	NDA	NDA	NDA
236	2106	441	NDA	0.0263	4.0	1.2	NDA
				Unit plugged. Solids were forced through as the pressure on filter increased.			

SAND FILTRATION STUDY AT OLD NEUTRALIZATION PIT

TABLE 2

Volume Treated	Aroclor Concentration of Influent (ppb) 1221	1242	1254	Average Daily Flow (GPM)	Aroclor Concentration of Effluent 1221	1242	1254
38	4100	4000	NDA	0.0263	-	-	-
76	8000	2750	NDA	0.0263	138	5	NDA
114				0.0263			
152	48000	36500	NDA	0.0263	-	-	-
190	2594	844	NDA	0.0263	157	12	NDA
228	1800	400	NDA		178	12	NDA

CARBON FILTRATION STUDY AT NEW PIT

TABLE 3

Volume Treated (Gal.)	Aroclor Concentration of Influent (ppb) 1221	1242	1254	Average Daily Flow (GPM)	Aroclor Concentration of Effluent (ppb) 1221	1242	1254
38	31	109	NDA	0.0263	NDA	2	NDA
76	4	40	NDA	0.0263	NDA	NDA	NDA
114	210	32	NDA	0.0263	NDA	NDA	NDA
152	340	4	NDA	0.0263	NDA	4	NDA

SAND FILTRATION STUDY AT NEW PIT

TABLE 4

Volume Treated (Gal.)	Aroclor Concentration of Influent (ppb) 1221	1242	1254	Average Daily Flow (GPM)	Aroclor Concentration of Effluent 1221	1242	1254
38	110	72	NDA	0.0263	48	3	NDA
76				0.0263	-	-	-
163	1200	820	NDA	0.0605	NDA	NDA	NDA
277	260	60	NDA	0.079	NDA	NDA	NDA
364	840	150	NDA	0.0605	7	NDA	NDA
446	610	180	NDA	0.057	60	NDA	NDA
516	NDA	560	NDA	0.0482	55	NDA	NDA

TSD - Anniston (JCLandwehr)

PR&D work on PCB removal from waste water is continuing. The final report on PCB removal by sand filtration will be issued 1-8-71. The carbon adsorption studies of the Aroclor sump effluent have continued for three months with removal to less than 10 ppb in the first of 4 five-foot long columns. The experimental work will be terminated and reported as soon as the Monsanto-vendor (Calgon Corporation) development of scale-up factors is complete. The reactor-clarifier studies to evaluate PCB removal by addition of a cheap solid adsorbent (such as clay, limestone, etc.) followed by solids removal by flocculation-clarification are targeted to begin by 2-1-71.

Environmental Studies-Monsanto Europe

During a visit to B.I.C.C. at Helsby we introduced MCS.1016 as a potential replacement product for Aroclor 1242. In a general discussion on pollution problems, with the Technical Manager, it was clear that BICC are anxious to co-operate. They will also look for any technical improvements which MCS.1016 might provide and report to on the results of the trials.

There has been some U.K. press reaction to the publication in 'Nature' of the report by A.V. Holden, at Pitlochry, that PCBs are present in sewage sludge which is being dumped in the Clyde and Thames estuaries. This is the report on the work which Holden described to us last May. The 'Guardian' report links this with the bird-kill in the Irish Sea in late 1969. We are still awaiting the draft of the NERC report on that incident. The PCB story has now been superseded, at least temporarily, in the U.K. press by the "mercury in tuna fish"scare.

Biodegradation-Monsanto Europe

We have still failed to degrade the 2,3,3'4,5-pentachloro biphenyl using the C_2 organism, using a technique similar to that used successfully with the 2,2'3,3',4',5'-hexachlor biphenyl. Work is still continuing with this and with 4,4'-dichlor biphenyl.

A new soil culture (C_3), claimed by workers at University College, Bangor, to degrade biphenyl by a different mechanism from C_2, has been used to degrade Aroclor 1242 and MCS.1016. Preliminary results confirm that degradation occurs, but we do not yet have information on the pattern of degradation.

Work is progressing on the analytical procedures for quantification and identification of residues. We are now able to identify a number of peaks and by a process of elimination suggest probable identification of other components. We hope to give figures for quantifying total residues in degraded Aroclor 1242 and MCS.1016 during the next few weeks. This information will be extremely useful in "selling" MCS.1016 against competitive products.