

DR. 2292

**Acid in Perchloroethylene Scrubber
Solutions Used in HTGR Fuel Preparation
Processes. Analytical Chemistry Studies**

D. A. Lee

OAK RIDGE NATIONAL LABORATORY
OPERATED BY UNION CARBIDE CORPORATION · FOR THE DEPARTMENT OF ENERGY

MASTER

ORNL/TM-6750
Dist. Category UC-77

Contract No. W-7405-eng-26
Purchase Order 64357AG

ANALYTICAL CHEMISTRY DIVISION

Consolidated Fuel Recycle Program - Refabrication
(DOE Activity AG 20 40 04 5)

ACID IN PERCHLOROETHYLENE SCRUBBER SOLUTIONS USED IN HTGR
FUEL PREPARATION PROCESSES. ANALYTICAL CHEMISTRY STUDIES

D. A. Lee

Date Published - February 1979

NOTICE: This document contains information of a preliminary nature. It is subject to revision or correction and therefore does not represent a final report.

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37830
operated by
UNION CARBIDE CORPORATION
for the
DEPARTMENT OF ENERGY

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

UNCLASSIFIED BY 60320 UCBAW/MLG/UCBAW/MLG

14

CONTENTS

	<u>Page</u>
Abstract	1
Introduction	1
Experimental	4
Results and Discussion	5
Conclusions	9
Acknowledgments	10
References	11

ABSTRACT

Acids and corrosion products in used perchloroethylene scrubber solutions collected from HTGR fuel preparation processes have been analyzed by several analytical methods to determine the source and possible remedy of the corrosion caused by these solutions. Hydrochloric acid was found to be concentrated on the carbon particles suspended in perchloroethylene. Filtration of carbon from the scrubber solutions removed the acid corrosion source in the process equipment. Corrosion products chemisorbed on the carbon particles were identified. Filtered perchloroethylene from used scrubber solutions contained practically no acid.

It is recommended that carbon particles be separated from the scrubber solutions immediately after the scrubbing process to remove the source of acid and that an inhibitor be used to prevent the hydrolysis of perchloroethylene and the formation of acids.

 INTRODUCTION

Microspheres of high-temperature gas-cooled reactor (HTGR) fuel are coated with pyrocarbon and silicon carbide by chemical-vapor-deposition (CVD) processes. Pyrocarbon coatings are deposited on the fuel kernels in fluidized-bed processes by the pyrolysis of acetylene and propene at 1200-1400°C. Silicon carbide CVD results from the pyrolysis of methyltrichlorosilane (CH₃SiCl₃) in the presence of hydrogen at ~1500°C. These coating processes have been described.¹

The chemical reactions, in simplified form, are presented in the following equations:



The pyrolysis of acetylene (Eq. 1) and propene (Eq. 2) produces a large number of precursor compounds, which may be swept into the effluent stream before they completely decompose into carbon and hydrogen. The pyrolysis

of CH_3SiCl_3 (Eq. 3) produces copious quantities of hydrogen chloride, which is very soluble in any available water, producing hydrochloric acid.

Condensable gases and entrained particles are scrubbed from the effluent gas stream by perchloroethylene.²⁻³ The scrubber (Fig. 1) consists of a reservoir of perchloroethylene, which is pumped through spray nozzles in a column, co-current with the effluent stream, and collected again in the reservoir. The scrubber solution accumulates fine particles of carbon, dissolved hydrocarbons, water, and acid. This scrubber solution is stored in the reservoir and is used repeatedly for several days to months before it is replaced by fresh perchloroethylene.

The acid in the used scrubber solution has been found to be very corrosive in the perchloroethylene recovery system. It attacks stainless steel and other metal parts in the equipment and was the impetus for making this study. The most probable source of this acid is hydrogen chloride (released from the decomposition of methyltrichlorosilane) combining with water, which has been condensed in the scrubber solution, thus producing hydrochloric acid. Normally, water should not be present in oxygen-free systems; however, the coating facility has been used for uranium weak acid resin carbonization, which is a source of water, both from the dehydration of uranyl ions and from the reaction of UO_3 or U_3O_8 with hydrogen or any hydrocarbon. Water may also be produced in the conversion of UO_2 to UC_2 in the presence of hydrogen. In the early stages of conversion, hydrogen is always present (from the last stages of carbonization) and may react with CO from $\text{UO}_2 + \text{C} \xrightarrow{\Delta} \text{UC}_2 + 2\text{CO}\uparrow$ in a Fischer-Tropsch reaction:⁴ $n\text{CO} + (2n + 1)\text{H}_2 \rightarrow \text{C}_n\text{H}_{2n+2} + n\text{H}_2\text{O}$. Also, between coating runs, water from the atmosphere may collect on the graphite components in the process equipment. Carbon surfaces which have been subjected to high temperatures have a high affinity for water when cooled.

Another possible source of acid in perchloroethylene is the oxidation and hydrolysis of perchloroethylene to produce HCl and trichloroacetic acid.⁵ This may be more of a problem from redistilled perchloroethylene, which does not contain an inhibitor.⁶⁻⁷ The degree of hydrolysis is increased with temperature and with increasing water concentration. The presence of metals catalyze the reaction, i.e., $\text{Al} < \text{steel} < \text{Cu}$. Hydrolysis products include Cl_3CCOOH , Cl_3CCOCl , C_2HCl_3 , COCl_2 , CCl_4 , CHCl_3 , HCl , CO , and CO_2 .⁸

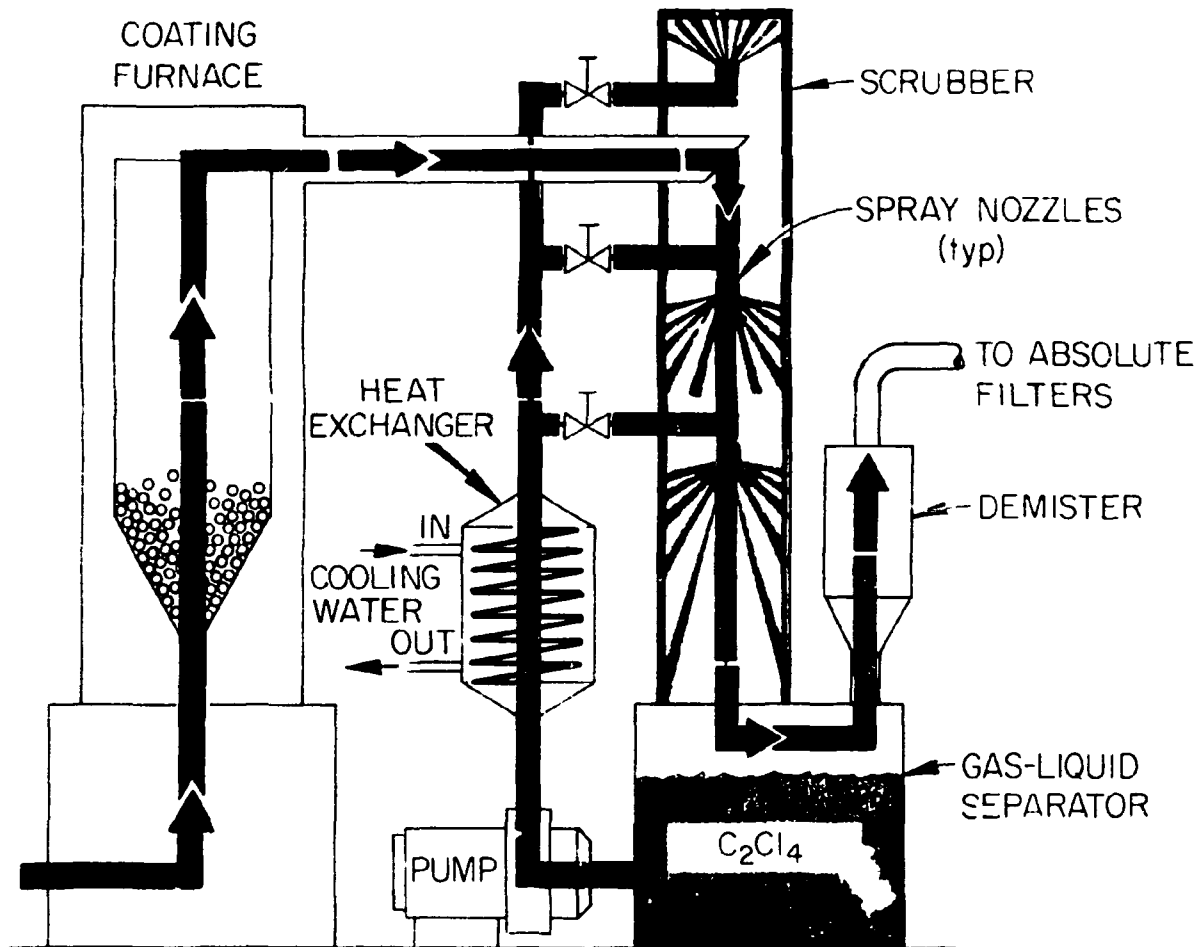


Fig. 1. Perchloroethylene scrubber for removing soot and hydrocarbons from coater effluent

Several techniques have been used to identify and quantify reaction products which produce corrosion or are the products of corrosion. To determine acid in perchloroethylene, a nonaqueous titration method was developed. Water in perchloroethylene was determined by Karl Fischer titration. Acid in aqueous leach solutions of carbon filtered from scrubber solutions was titrated to a pH endpoint with sodium hydroxide. Metals present in the carbon were determined by emission spectrometry. Free acid in aqueous leach solutions of carbon was determined by enthalpimetric titration. Chloride in the aqueous leach solutions was determined by titrimetry.

EXPERIMENTAL

Attempts to extract acid from perchloroethylene with water or sodium hydroxide solution were not successful because of emulsions, and the presence of suspended carbon made quantitative separation of the immiscible phases difficult. Therefore, the determination of acid in the organic phase directly seemed advantageous. Nonaqueous acid titrimetry has been developed.⁹⁻¹⁰ The first base chosen to titrate acid in perchloroethylene was tetrabutylammonium methoxide in 90% benzene-10% methanol, but being an extremely strong base, it promoted the hydrolysis of perchloroethylene to form acids. A less reactive titrant, KOH in 10% glycol-90% methanol, was found to work satisfactorily. The titration solvent medium was pyridine, which had good acidity potential properties.¹¹ The electrodes which produced sharp potential endpoints were anodized platinum as the indicating electrode and cathodized antimony as the reference electrode.¹⁰

The Karl Fischer method was used for water determination, and the Volhard method for chloride. These methods are described in the ORNL Master Analytical Manual, Nos. 1 230045 and 1 212020, respectively.

Enthalpimetric titration analysis was used to determine free acid in the aqueous leach of the carbon particles suspended in the perchloroethylene solutions. Iron, chromium, nickel, uranium, and copper ions in the leach solutions were complexed by potassium fluoride, and the titration made with sodium hydroxide; the method was similar to that described by Bodewig.¹²

RESULTS AND DISCUSSION

Filtered perchloroethylene was titrated by the nonaqueous titration method, and the amount of acid determined. Results of some selected samples are given in Table 1.

Table 1. Molarity of acid found in filtered perchloroethylene

Sample ^a	<i>M</i> , first potential break	<i>M</i> , second potential break
Scrubber solution removed 2/10/78	0.00009	
DR-2B	0.00006	
DR-1-recycled	0.00000	
DR-2A (top layer)	0.00000	
CTII	0.00006	
J-1	0.00002	
CTI	0.00034	0.0024
J-3	0.000006	0.0024

^aDR-2B = drum of used perchloroethylene from carbon coating and carbonization process—bottom layer.

DR-1-recycled = drum of redistilled perchloroethylene.

DR-2A = drum of used perchloroethylene from carbon coating and carbonization process—top layer.

CTII = recycled perchloroethylene used for metal corrosion test II.

J-1 = jar of used dirty perchloroethylene from coating facility.

CTI = corrosion test using dirty perchloroethylene from carbonization process.

J-3 = jar of dirty perchloroethylene similar to J-1.

These results show that very little acid was present in the filtered perchloroethylene. Two of the samples titrated exhibited two inflection points or potential breaks in the titration curves (Fig. 2). These inflection points suggest that either a dibasic acid or two acids of different dissociation constants were present.

Some of the used perchloroethylene scrubber solutions contained so much water that they separated into two phases. These water phases were titrated for acid using aqueous sodium hydroxide as the titrant. The potentiometric endpoint was determined with a pH meter having glass and calomel electrodes. Three samples from DR-2 (A, B, and C) had the following

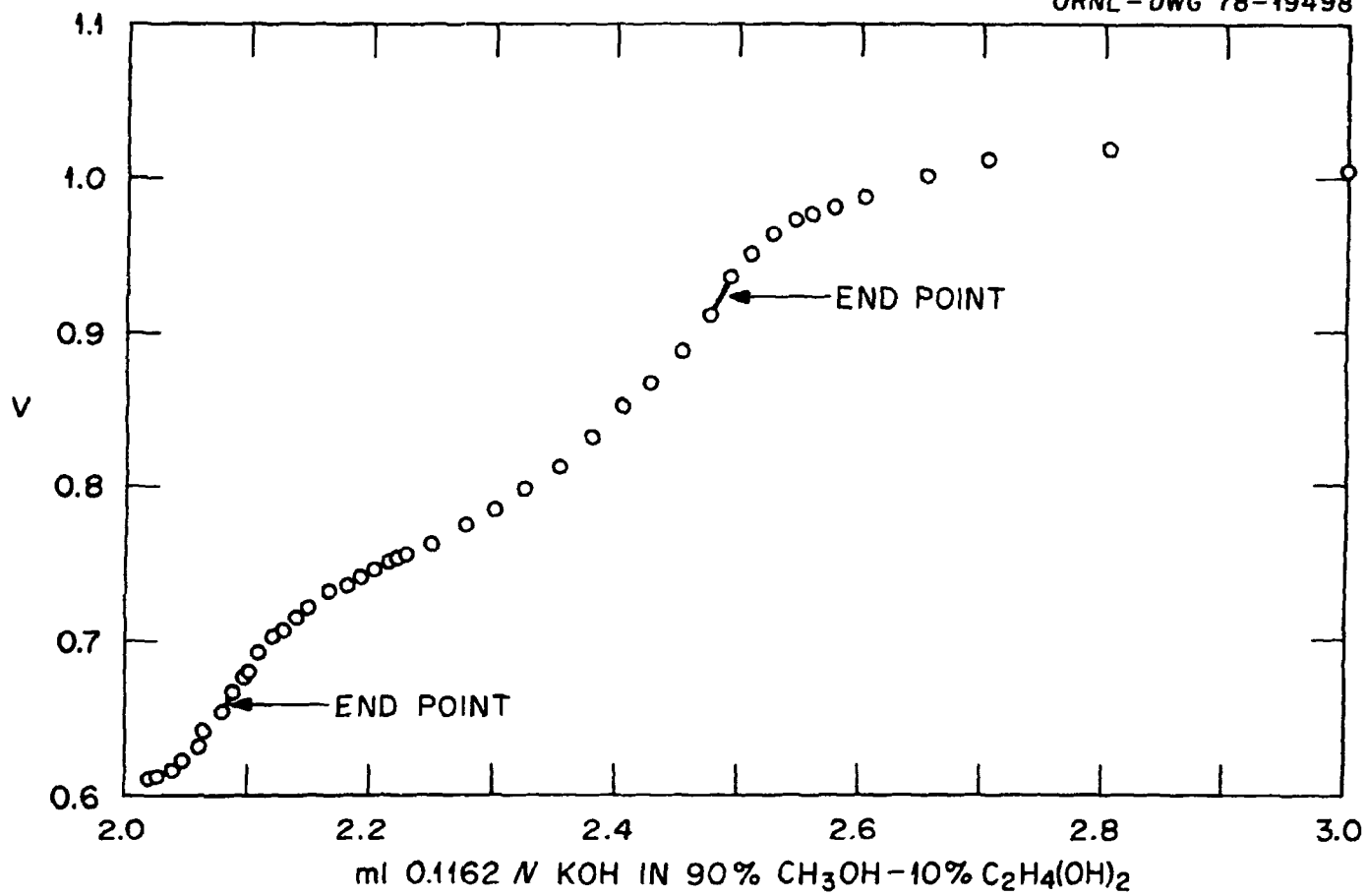


Fig. 2. Titration of acids in dirty perchloroethylene (CTI)

acid molarities: A = 0.0132, B = 0.0132, and C = 0.0176. These titration curves had only one inflection point. These results show that acid concentrates in the aqueous phase.

Some perchloroethylene samples free of suspended carbon were analyzed for water by the Karl Fischer method: J-1 "bottoms," 0.010%; J-3, 0.0043%; CTI, 0.011% H₂O. These results are in agreement with the reported solubility of water in perchloroethylene, 0.0104 wt % at 30°C.¹³ However, the analysis of a perchloroethylene sample containing suspended carbon yielded 0.142% H₂O, while the same solution with carbon removed contained only 0.002% H₂O. It was concluded that water concentrated on the carbon. Consequently, it was plausible to conclude that acid was also concentrated on the carbon.

Dirty perchloroethylene removed from the scrubber on August 16, 1978, was treated as follows. Fifty ml of perchloroethylene slurry was filtered through a medium-porosity glass frit. The collected carbon was washed twice with petroleum ether. The carbon (2.33 g) was then leached four times with hot water, and the leach solutions collected and adjusted to 100 ml with water. Aliquots of the leach solution were titrated potentiometrically using a pH meter and sodium hydroxide as the titrant. The titration curves had two potential breaks (Fig. 3). The average values were 0.0155 *M* at the first break and 0.0308 *M* at the second, relative to the original 50-ml test sample. Also, an enthalpimetric titration of the free acid was made on the same aqueous solution from the leaching of carbon filtered from the dirty perchloroethylene sample (8/16/78). Potassium fluoride was used to complex the hydrolyzable cations present. The titration was made with sodium hydroxide. Two aliquots were titrated and were determined to contain 0.014 and 0.016 *M* acid relative to the 50-ml original perchloroethylene solution. These results suggest that the first break in the potentiometric titration curve obtained in the absence of KF was due to free acid. The second break observed may be due to the acidity produced by the hydrolysis of the cations present in the leach solution.¹⁴

The cations present in the total aqueous leach solution of carbon from 50 ml of dirty perchloroethylene slurry (8/16/78) were precipitated with ammonium hydroxide, ignited at 800°C, and weighed. The mixed oxides collected weighed 0.0446 g. An emission spectrographic analysis of this

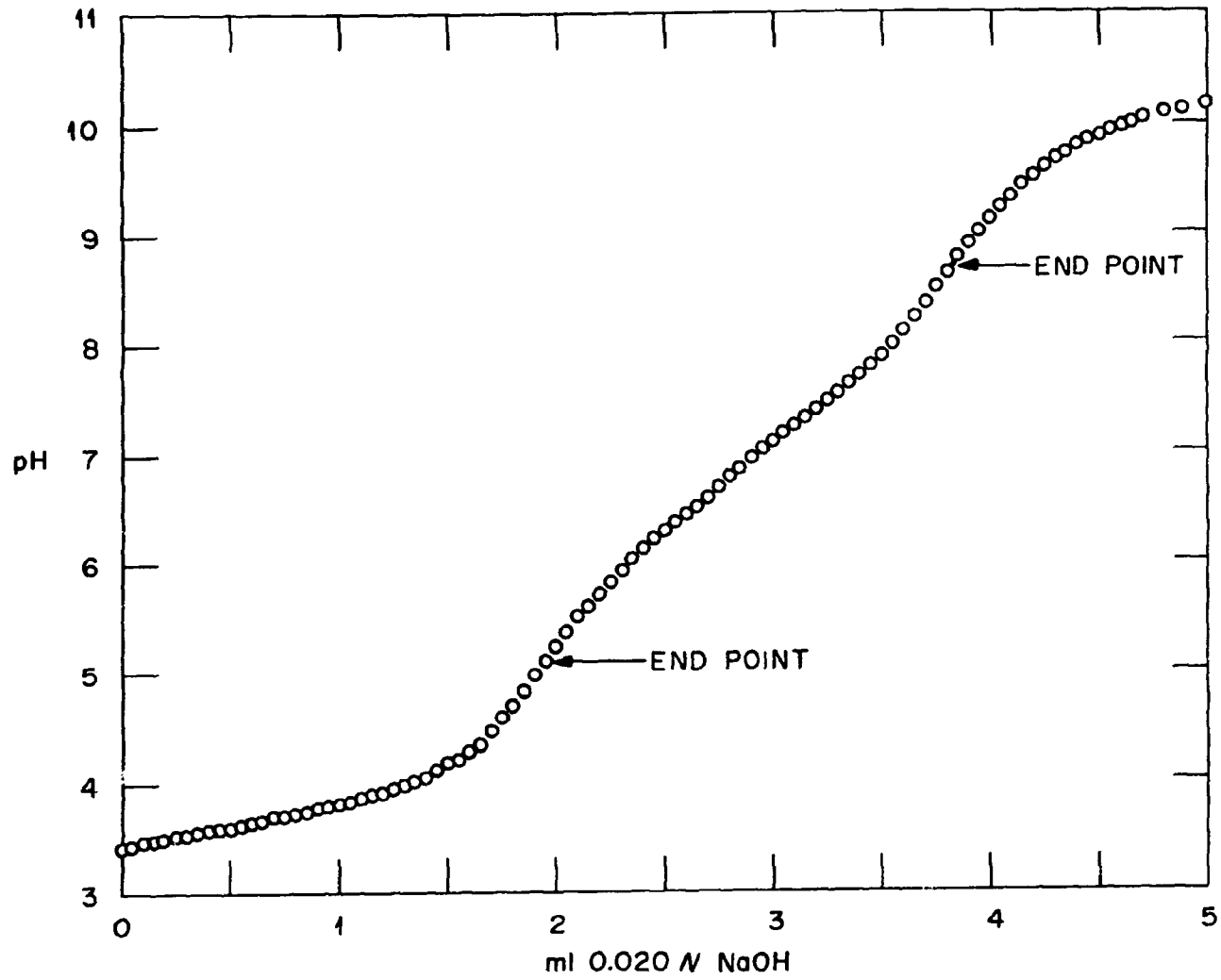


Fig. 3. Titration of a water leach solution of carbon filtered from dirty perchloroethylene

material had the following composition: Fe ≥ 10 , Cr ~ 3 , Si ~ 3 , U ≥ 1.0 , Ni 1, Mn 1, Na 1, Ca 0.8, Mg 0.7, Al 0.3, Ba 0.3, Co 0.3, Cd 0.2, Cu 0.2, Mo 0.2, Sr 0.2, Zr 0.2, and Ta 0.1 wt %. This amount of mixed oxides in the leach solution was approximately equivalent to the amount of acid present (using Fe_2O_3 as the formula weight for mixed oxides). Therefore, the acid indicated by the second potentiometric break must be associated with the metal salts present. The leached carbon residue was ignited, and it contained metal oxides. Emission spectrographic results for these ignited oxides are as follows: Si > 10 , Fe 5, Cr 0.7, B 0.3, Cu 0.3, Al 0.2, Na 0.2, and Ni 0.2 wt %.

The aqueous leach of the filtered carbon was analyzed for chloride by the Volhard method. The chloride content was 0.018 *M* relative to 50 ml of dirty perchloroethylene. This figure agrees well with the concentration of acid in the first potential break; thus, the acid may be presumed to be HCl.

CONCLUSIONS

Acid is contained in perchloroethylene solutions used to scrub the effluent gases and soot from microsphere fuel preparation processes in which methyltrichlorosilane is used as a reactant. This acid concentrates in water produced by various chemical reactions or from the atmosphere during storage. The aqueous acid solutions, in turn, concentrate on the suspended carbon particles. The acid is principally HCl, some of which reacts and corrodes metal surfaces in the process equipment.

From this study it is recommended that the carbon particles be filtered from the scrubber solutions, either during the scrubbing process or immediately afterward. This procedure would remove the majority of the acid present and minimize the corrosion problem.

The oxidation and subsequent hydrolysis of perchloroethylene do not appear to be major contributions to the acid corrosion problem. It is recommended that an inhibitor such as thymol⁶ be used in the scrubber solutions at all times to prevent the hydrolysis of perchloroethylene and the subsequent formation of acids. Or, it may be advantageous to add an amine, soluble in perchloroethylene, to neutralize any acid present; a tertiary amine such as Adogen 364* is recommended.

*Ashland Chemical Company, Columbus, Ohio.

ACKNOWLEDGMENT

This problem was suggested by Sue Tiegs. She and Marilyn Hendricks (both of the Metals and Ceramics Division) supplied the samples for these studies, and their cooperation is appreciated. Many of the analyses were performed by our General Analytical Laboratory under the supervision of R. R. Rickard and our Mass and Emission Spectrometry Section under the supervision of J. A. Carter. J. L. Marley performed the enthalpimetric titrations. Thanks are given to D. A. Costanzo for helpful suggestions and to Donna Watson for preparing the manuscript.

REFERENCES

1. W. J. Lackey, D. P. Stinton, and J. D. Sease, "Improved Gas Distributor for Coating High-Temperature Gas-Cooled Reactor Fuel Particles," Nucl. Tech. 35, 227 (1977).
2. W. J. Lackey, J. D. Jenkins, F. J. Homan, and R. S. Lowrie, "Assessment of Coater Size for the Fuel Refabrication Prototype Plant," ORNL/TM-4567 (1974).
3. M. S. Judd, J. E. Van Cleve, Jr., and W. T. Rainey, Jr., "Recovery of Perchloroethylene Scrubbing Medium Generated in the Refabrication of High-Temperature Gas-Cooled Reactor Fuel," ORNL/TM-5620 (1976).
4. D. A. Lee, et al., "In-Line Monitoring of Effluents from High-Temperature Gas-Cooled Reactor Fuel Particle Preparation Processes by Mass Spectroscopy," Nucl. Tech. 34, 89 (1977).
5. K. C. Bailey and W. S. E. Hickson, "The Formation of Trichloroacetic Acid from Perchloroethylene by Atmospheric Oxidation," J. Chem. Soc. 1941, 145.
6. K. C. Bailey, "The Retardation of Chemical Reactions. Part IX. The Stabilization of Perchloroethylene for Medicinal Purposes," J. Chem. Soc. 1939, 767.
7. A. L. Lotts and P. R. Kasten, "Gas-Cooled Reactor Programs High-Temperature Gas-Cooled Reactor Fuel Recycle Development Annual Progress Report for Period Ending Sept. 30, 1977," ORNL-5423, p. 180 (September 1978).
8. V. D. Simonov, T. M. Shamsutdinov, V. E. Pogulyai, and L. G. Shcherbakova, "Study of the Hydrolysis of Tetrachloroethylene," Zn. Prikl, Khim. 49(7), 1650-2 (1976).
9. J. Kucharsky and L. Safarik, "Neutralization Titrations," Titration in Non-Aqueous Solvents, Elsevier Publishing Co., Amsterdam, pp. 125-129 (1965).
10. D. A. Lee, "Nonaqueous Microtitration of Dibenzoylmethane and Other Weak Acids," Anal. Chem. 38, 1168 (1966).
11. H. B. Van der Heijde, "Potentiometric Titrations in Non-Aqueous Solution. III. Directions for Choosing Solvent-Titrant Combinations," Anal. Chim. Acta 17, 512 (1957).
12. F. G. Bodewig, "Enthalpimetric Titration of Free Acid in Simulated Nuclear Fuel Solutions Containing Thorium and Other Hydrolyzable Ions," Anal. Chem. 46, 454 (1974).
13. V. D. Simonov, V. E. Pogulyai, and T. M. Shamsutdinov, "Solubility of Water in Certain Fully Chlorinated Derivatives of Hydrocarbons," Russ. J. Phys. Chem. 44, 1755 (1970).

14. H. Kubota and D. A. Costanzo, "Reactions in Concentrated Lithium Chloride Solution. Determination of Free Acid and Hydrolyzable Cation," *Anal. Chem.* 36, 2454 (1964).

INTERNAL DISTRIBUTION

- | | |
|-------------------------|---------------------------------------|
| 1. E. J. Allen | 27. A. P. Malinauskas |
| 2. P. Angelini | 28. J. L. Marley |
| 3. R. L. Beatty | 29. W. H. Miller |
| 4. R. J. Beaver | 30. K. J. Notz |
| 5. J. Begovich | 31. A. R. Olsen |
| 6. R. A. Bradley | 32. A. E. Pasto |
| 7. A. J. Caputo | 33. R. R. Rickard |
| 8. J. A. Carpenter, Jr. | 34. A. D. Ryon |
| 9. J. A. Carter | 35. W. D. Shults |
| 10. J. H. Coobs | 36. D. P. Stinton |
| 11. L. T. Corbin | 37. R. R. Suchomei |
| 12. D. A. Costanzo | 38. V. J. Tennery |
| 13. R. G. Donnelly | 39. S. M. Tiegs |
| 14. W. P. Eatherly | 40. T. N. Tiegs |
| 15. D. E. Ferguson | 41. D. B. Trauger |
| 16. P. A. Haas | 42. J. S. Vavruska |
| 17. W. R. Hamel | 43. V. C. A. Vaughen |
| 18. F. E. Harrington | 44. J. E. Van Cleve |
| 19. C. C. Haws | 45. J. R. Weir |
| 20. M. S. Hendricks | 46. R. G. Wymer |
| 21. F. J. Homan | 47-49. Central Research Library (3) |
| 22. D. R. Johnson | 50. Document Reference Section |
| 23. P. R. Kasten | 51-60. Laboratory Records Dept. (10) |
| 24. W. J. Lackey | 61. Laboratory Records Dept., ORNL RC |
| 25. A. L. Lotts | 62. ORNL Patent Office |
| 26. J. E. Mack | |

EXTERNAL DISTRIBUTION

- 63-66. DOE DIVISION OF NUCLEAR POWER DEVELOPMENT, Washington, D. C. 20545
Director
Assistant Director, Fuel Cycle
Chief, Technology Branch
Chief, Projects Branch
67. DOE IDAHO OPERATIONS OFFICE, P. O. Box 2108, Idaho Falls, ID 83401
Barry Smith
68. SAN-DEVELOPMENT, SAN DIEGO AREA OFFICE, P. O. Box 81325, San Diego, CA 92138
Senior Program Coordinator
- 69-71. DOE OAK RIDGE OPERATIONS OFFICE, P. O. Box E, Oak Ridge, TN 37830
Office of Assistant Manager, Energy Research and Development
Director, Reactor Division
F. E. Dearing, Reactor Division
- 72-248. DOE TECHNICAL INFORMATION CENTER, P. O. Box 62, Oak Ridge, TN 37830
For distribution as shown in TID-4500 Distribution Category, UC-77,
Gas-Cooled Reactor Technology
(25 copies—NTIS)