CONF-910981--2

WHC-SA-1209-FP

Destruction of Complexants Used in Groundwater Decontamination

Prepared for the U.S. Department of Energy
Office of Environmental Restoration
and Waste Management

Westinghouse
Hanford Company Richland, Washington

Hanford Operations and Engineering Contractor for the
U.S. Department of Energy under Contract DE-AC06-87RL10930

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DE91 018139

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Date Published
August 1991

To Be Presented at
Environmental Remediation 1991
Pasco, Washington
September 8-11, 1991

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DESTRUCTION OF COMPLEXANTS USED IN GROUNDWATER DECONTAMINATION

K. M. Hodgson
T. P. Moberg

ABSTRACT

A supported liquid membrane process is being developed to remove uranium from aqueous solutions. The uranium would be concentrated into a strip solution containing either vinylidene-1,1-diphosphonic acid (VDPA) or 1-hydroxyethane-1,1-diphosphonic acid (HEDPA). This study compares the degradation of HEDPA and VDPA under similar conditions. For the time of the tests in this study (3 h) the maximum amount of HEDPA that was destroyed was 83.5% using hydrogen peroxide and the maximum amount of VDPA destroyed was 64.6% using nitric acid.

INTRODUCTION

A new class of reagents for use in nuclear waste processing was developed by the chemical division at the Argonne National Laboratory (ANL). These reagents, which are substituted methane diphosphonic acids, have been referred to as thermally unstable complexants (TUC).[1,2]

The TUCs possess a unique combination of properties that include: organic complexes that are highly stable in very acidic media, metal ion complexes that are aqueous soluble, and the ability to readily decompose to innocuous substances when heated in the presence of moderate oxidizing agents. Some of the major applications of TUCs are the stripping reagent in solvent extraction and ion exchange processes, holdback reagent in strontium and cesium extraction processes, and decontamination reagent.

The reagents evaluated in this study, which are substituted methane diphosphonic acids, were vinylidene-1,1-diphosphonic acid (VDPA) and 1-hydroxyethane-1,1-diphosphonic acid (HEDPA). The VDPA, developed by ANL as a TUCs, is not readily available. The ability to decompose HEDPA, which was not developed by ANL, was discovered after the development of TUCs. The HEDPA is readily available and could possibly be used in a supported liquid membrane process as a stripping solution for uranium.

The purpose of this study was to compare the degradation of HEDPA and VDPA using degradation conditions for VDPA similar to those developed by ANL. The conditions used for the degradation of VDPA and HEDPA included temperature change (25 °C, 60 °C, and 95 °C), an oxidant (H_2O_2) with a sodium orthovanadate catalyst at 25 °C and 60 °C, and adjustment of the pH to less than 1 by adding HNO_3 at 25 °C, 60 °C, and 95 °C.

The possible decomposition products for HEDPA and VDPA were phosphoric acid (H_3PO_4) and carbon dioxide (CO_2). The method used to characterize the decomposition of the complexants was ion chromatography.

PHYSICAL DESCRIPTION AND THEORY

Theory

The TUCs complexants developed by the chemical division at ANL are substituted methane diphosphonic acids. These complexants can be used for the aqueous complexation of transition metals, lanthanides, and actinides found in nuclear waste. Figure 1 shows a substituted methane diphosphonic acid in the general sense. The X and Y are used to adjust the lability of the C-P bond to oxidation, increase the acidity of the $-PO(OH)_2$, and increase the water solubility of the complexes.

Place Fig. 1 here.

Physical Description

Figure 2 gives the structure, name, and acronym for both complexants that were used in the testing.

The VDPA solution was obtained from a supported liquid membrane demonstration in which natural uranium was removed from a synthetic groundwater feed. The conditions and extent of decomposition for the VDPA solution were characterized to establish the VDPA effectiveness as a complexant. Approximately 8 L of the 0.086$\underline{M}$ VDPA solution were available. For comparison, 3.9 L of 0.086$\underline{M}$ HEDPA solution were made.

TEST APPROACH

Each test was done in a glass beaker and continuously stirred. The amount of VDPA, HEDPA, H_2O_2, HNO_3, and Na_3VO_4 that were used in making the chemical mixtures for each test are given in Table I. Each mixture was made at atmospheric conditions. Some of the tests required that the samples be heated on a hot plate.

Table II shows the conditions that were tested for the degradation of the VDPA and HEDPA complexants. These conditions included temperature variation, oxidation using hydrogen peroxide (0.504 g$\underline{M}$ H_2O_2) with a sodium orthovanadate catalyst (5.44×10^{-4} g$\underline{M}$ Na_3VO_4), and pH adjustment to less than 1 by nitric acid (1.234 g$\underline{M}$ HNO_3) addition.

Place Fig. 2 here.

Table I. Chemical Mixtures.

Test Numbers	VDPA 0.086M (ml)	HEDPA 0.086M (ml)	H_2O_2 30% (ml)	HNO_3 70.4% (ml)	Na_3VO_4 (g)
1,3,5	500	-	-	-	-
2,4,6	-	500	-	-	-
7,9	488	-	40	-	-
8,10	-	488	40	-	0.1
11,13,15	448	-	-	74	-
12,14,16	-	448	-	74	-

Table II. Test Matrix of Degradation Conditions.

Test No.	Complexant	Temp (°C)	Oxidant	pH Adjust	Catalyst ($NaVO_4$)
1	VDPA	RM	--	-	-
2	HEDPA	RM	--	-	-
3	VDPA	60	--	-	-
4	HEDPA	60	--	-	-
5	VDPA	95	--	-	-
6	HEDPA	95	--	-	-
7	VDPA	RM	H_2O_2	-	-
8	HEDPA	RM	H_2O_2	-	yes
9	VDPA	60	H_2O_2	-	-
10	HEDPA	60	H_2O_2	-	yes
11	VDPA	RM	--	yes	-
12	HEDPA	RM	--	yes	-
13	VDPA	60	--	yes	-
14	HEDPA	60	--	yes	-
15	VDPA	95	--	yes	-
16	HEDPA	95	--	yes	-

The H_2O_2 was added in two parts because of the slow reaction rate. The first half was added initially and the second half was added an hour later.

Tests 7 and 9 with VDPA required no catalyst, since the uranium in the solution acted as the catalyst. Tests 8 and 10 with HEDPA required catalyst addition because there was no uranium in the solution to act as the catalyst. Sodium vanadate was added to obtain a vanadium concentration of $1.0 \times 10^{-5}\underline{M}$.

RESULTS

Test Solutions

Since the decomposition of the complexants yielded H_3PO_4 and CO_2 as the products, the amount of complexant degradation was determined by the concentration of free PO_4 in the final samples. The analysis of the degradated TUCs samples were completed using ion chromatography.

The VDPA and HEDPA degradation percentages are given in Tables III and IV. These percentages were found by calculating the amount of VDPA or HEDPA that corresponded to the free PO_4 present in each sample and then comparing the corresponding VDPA or HEDPA to the original concentrations. None of the VDPA or HEDPA complexants were completely decomposed during any of the tests. The total time for each test was 3 h. The highest degradation for VDPA occurred in test 15 with a 64.6 percent decomposition. The highest degradation for HEDPA occurred in test 10 with an 83.5 percent decomposition.

Table III. VDPA Degradation Percentages Calculated Using PO_4 Analytical Results.

Test No.	PO_4 (ppm)	PO_4 (wt%)	PO_4 (g)	VDPA (g)	Degradation (%)
1	692	0.069	0.34	0.35	4.3
3	773	0.077	0.31	0.32	3.8
5	5,292	0.529	0.85	0.88	10.5
7	4,424	1.442	2.36	2.42	29.7
9	7,682	0.768	3.20	3.27	40.2
11	1,149	0.115	0.63	0.65	8.6
13	1,510	0.151	0.76	0.78	10.5
15	16,980	1.698	4.72	4.83	64.6

Table IV. HEDPA Degradation Percentages Calculated Using PO_4 Analytical Results.

Test No.	PO_4 (ppm)	PO_4 (wt%)	PO_4 (g)	HEDPA (g)	Degradation (%)
2	55	0.006	0.02	0.03	0.3
4	79	0.008	0.03	0.03	0.4
6	390	0.039	0.04	0.04	0.5
8	10,210	1.021	5.46	5.93	68.9
10	13,980	1.398	6.61	7.18	83.5
12	712	0.071	0.39	0.42	5.4
14	694	0.069	0.33	0.36	4.6
16	2,169	0.217	0.51	0.56	7.1

Figure 3 shows test 1-6 using only temperature variation. Both HEDPA and VDPA display an increase in degradation with increasing temperature; however, all the tests had less than 11 percent degradation. Moreover, VDPA was affected more by temperature than HEDPA.

Figure 4 shows the effects of H_2O_2 addition and temperature increase in tests 7-10. The Na_3VO_4 catalyst was added to the HEDPA solutions. Increasing temperature increased degradation. Addition of the oxidant (H_2O_2) in tests 8 and 10 caused significantly more degradation of the HEDPA relative to VDPA.

Figure 5 shows the effects of HNO_3 addition and temperature increase in tests 11-16. Again, increasing temperature increased degradation. The results from ANL for decomposing VDPA indicated that decomposition occurred only at a low pH.[2] Adjusting the pH using HNO_3 decomposed the VDPA more than the HEDPA. At 95 °C, the VDPA was decomposed by 64.6 percent, while the HEDPA was decomposed by only 7.1 percent.

In test 15, a precipitate formed on the bottom of the glass beaker, possibly containing uranium phosphate. The precipitate was not analyzed. There was 0.0016 gM of natural uranium present in the VDPA solution used in test 15. A uranium phosphate precipitate, therefore, could have accounted for only 2.0 percent of the free phosphate.

CONCLUSIONS

The best degradation of HEDPA was attained using Na_3VO_4 as the catalyst and H_2O_2 as an oxidant at 60 °C. It is possible that increasing the temperature could result in complete degradation of the HEDPA complexant.

Place Fig. 3 here.

Place Fig. 4 here.

Place Fig. 5 here.

The best degradation of VDPA was attained using HNO_3 at 95 °C.

Increasing the temperature of the samples resulted in a definite increase in complexant degradation; however, increasing temperature alone degraded the complexants by only 10.5 percent at 95 °C for VDPA and 0.5 percent at 95 °C for HEDPA.

Using H_2O_2 as an oxidant with a catalyst (uranium for VDPA and vanadium for HEDPA) mixed with the complexants dramatically increased the degradation of both VDPA and HEDPA. The HEDPA decomposed more than VDPA. The VDPA degraded by 29.7 and 40.2 percent at 25 °C and 60 °C, respectively. The HEDPA degraded by 68.9 percent and 83.5 percent at 25 °C and 60 °C, respectively. Increasing the temperature of the HEDPA solution possibly could have resulted in almost complete degradation. The test matrix used was based on the conditions of decomposition employed by ANL.

At 95 °C, the VDPA degraded by 64.6 percent using the HNO_3 addition to adjust the pH. This was based on the amount of free PO_4 in solution. For all other tests with HNO_3 the degradation was less than 10.5 percent.

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Fig. 1. Substituted Methanediphosphonic Acids

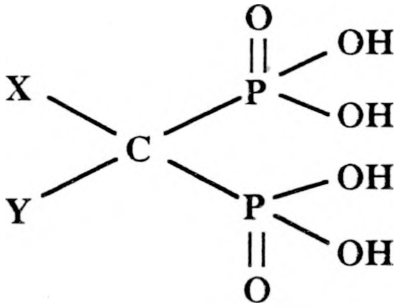


Fig. 2. Structure of the Organic Complexants

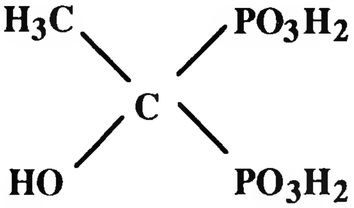
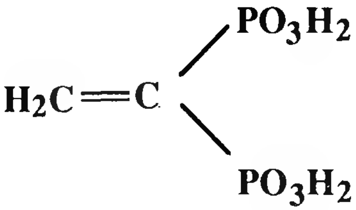
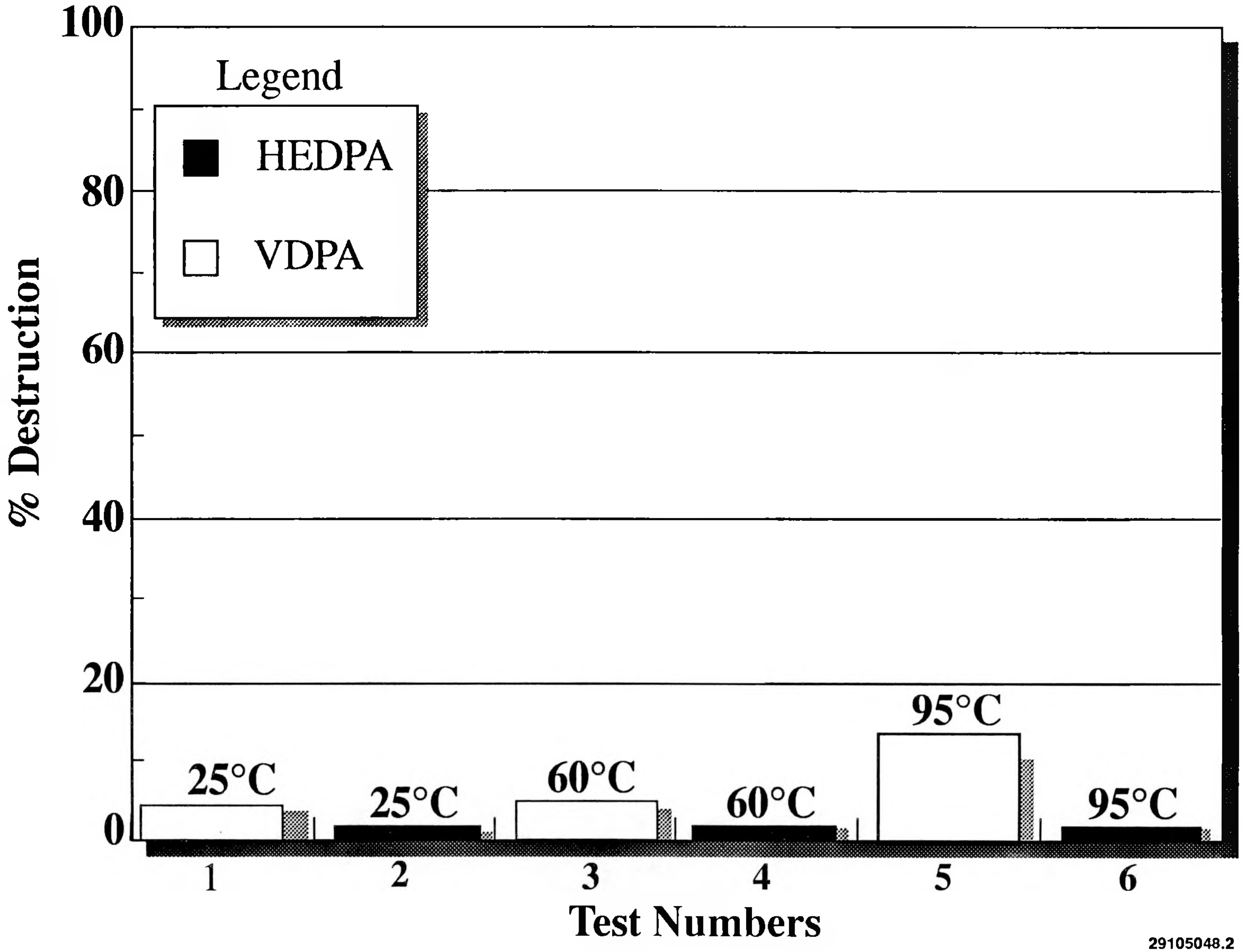
Structure	Name	Acronym
	1 - Hydroxyethane - 1, 1 - diphosphonic acid	HEDPA
	Vinylidene - 1, 1 - diphosphonic acid	VDPA

Fig. 3. Temperature Effect on Destruction



29105048.2

Fig. 4. Destruction with Peroxide Addition

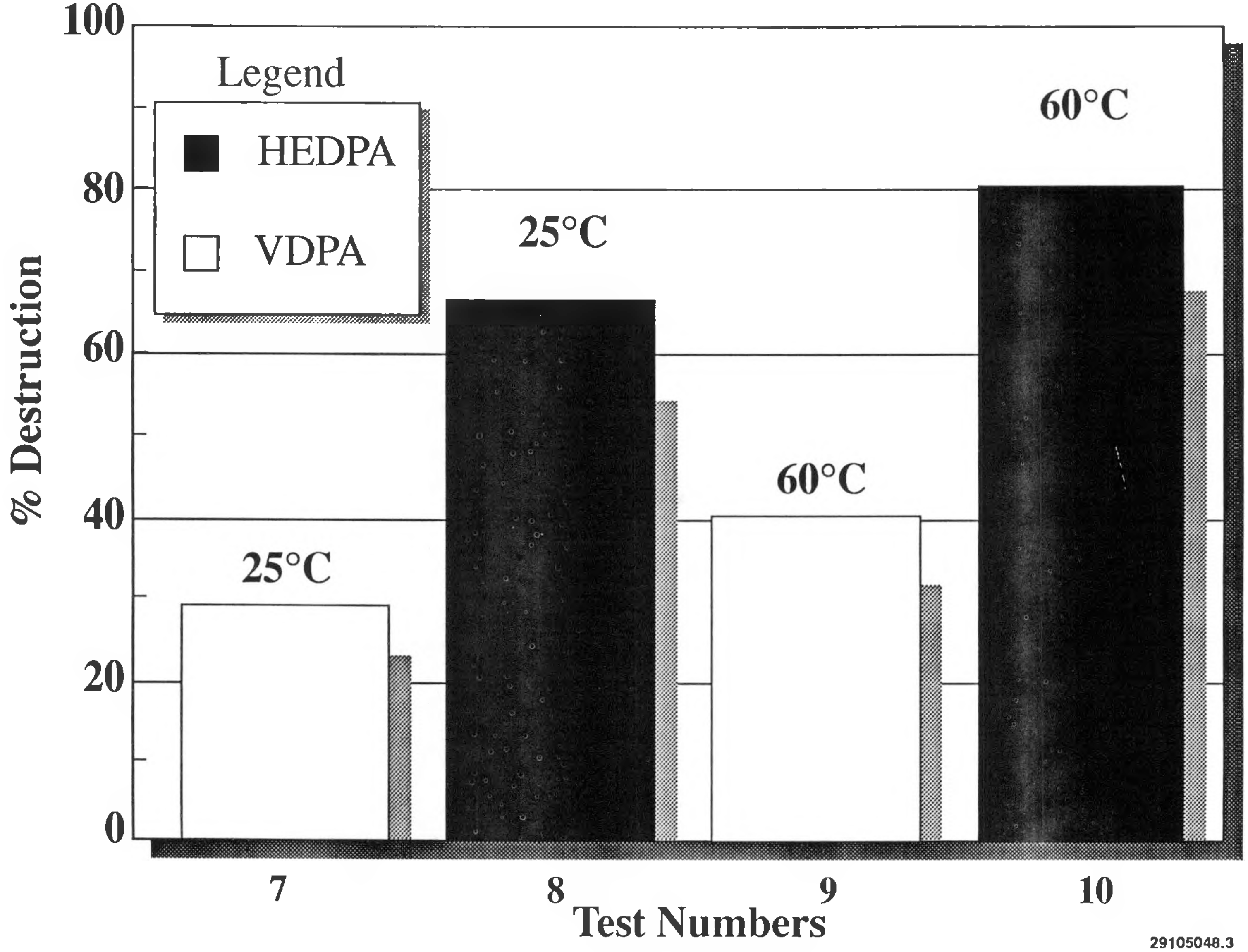


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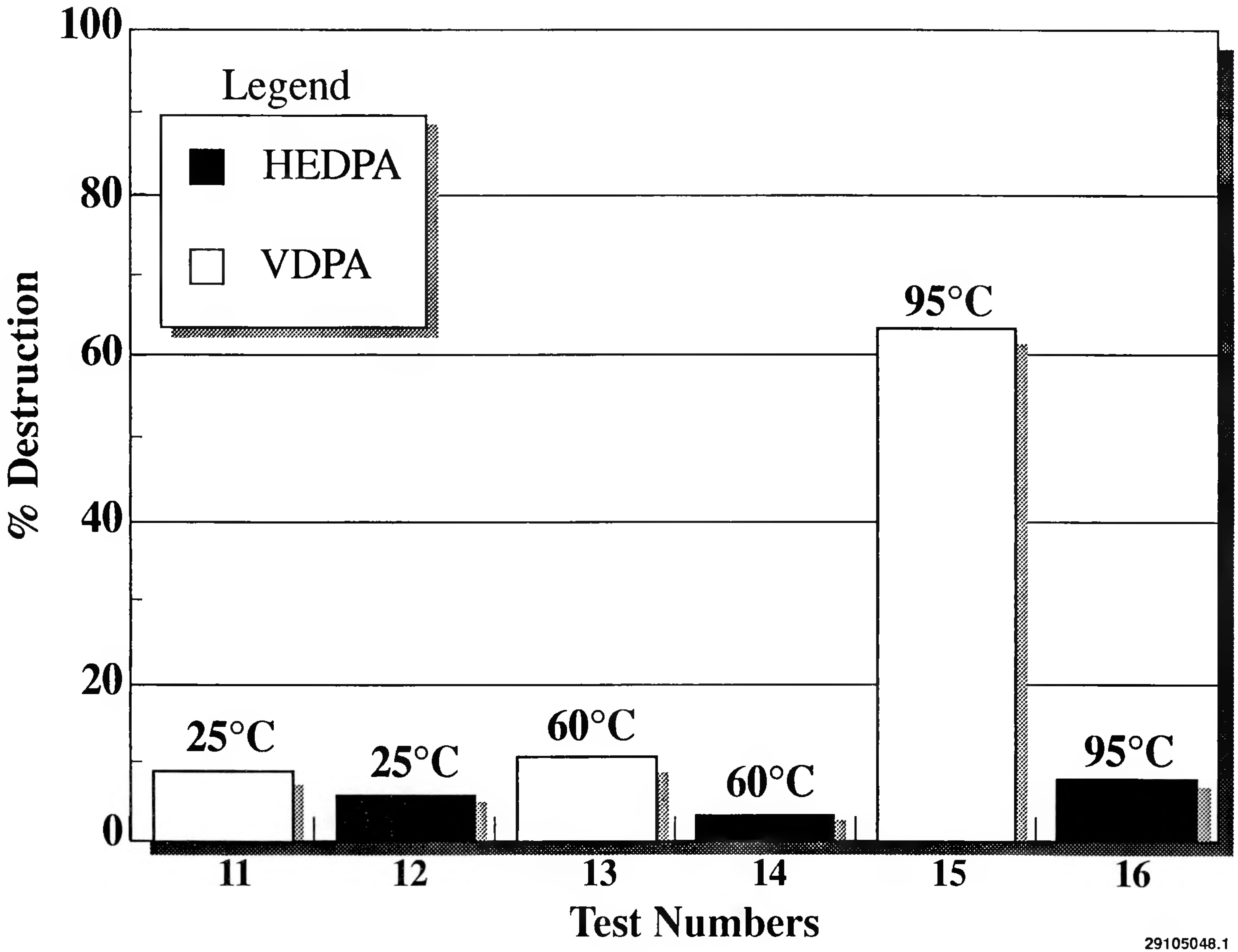
Fig. 5. Destruction with HNO_3 Addition



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