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CATALYTIC OXIDATION OF TRICHLOROETHYLENE AND PERCHLOROETHYLENE MIXTURES

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ABSTRACT

Catalytic oxidation is one of the demonstrated treatment alternatives currently available for treatment of air born contaminants. Halogenated hydrocarbons, however, have been difficult to treat by catalytic oxidation due to the poisoning effects of halogens on conventional catalysts. Improvements in catalyst technology using precious metal hybrid formulations have increased the capability to treat halogens. The recalcitrant nature of PCE has remained a challenge for catalytic treatment, until recently.

Allied Signal has recently developed a new formulation to address the challenge of oxidizing PCE. In January 1993 this new catalyst was installed and tested in an oxidizer at the Savannah River Site in South Carolina. The catalytic oxidizer was connected to a vapor extraction system treating a mixture of trichloroethylene (TCE) at a concentration of approximately 80 ppm and PCE at approximately 150 ppm.

Results of this operation verify the effectiveness of the new catalytic material in treating halogenated compounds in general, and PCE in particular.

CATALYTIC OXIDATION OVERVIEW

Catalytic Oxidation is a technology that has been used since the early 1970's for the control of volatile organic compounds (VOCs) emanating from a wide range of industrial applications. This technique involves heating the contaminated air to temperatures ranging from 500 to 900°F. The exact temperature depends on the contaminant to be removed. The heated air is passed over a catalytic material which causes the contaminants to oxidize them completely, at temperatures lower than would be possible with thermal oxidation

Typically the catalyst materials come from the noble metals group. Platinum has been commonly used either by itself or in combination with other noble metals. Palladium has also been used.

Title III of the 1990 Clean Air Act identifies 189 hazardous compounds as Air Toxics and requires implementation of control technologies to reduce their emissions. Of the 189 hazardous compounds, 154 can be oxidized catalytically. These compounds can be organized into four main categories:

Hydrocarbons	example: benzene
Halocarbons	example: trichloroethylene
Nitrogen Compounds	example: hydrogen cyanide
Oxygen Compounds	example: formaldehyde

Catalytic oxidation converts these compounds to safer end products (carbon dioxide, water vapor, nitrogen, oxygen, and hydrogen chloride).

Traditionally, catalysts have been vulnerable to deactivation from several groups of poisons. One of these groups, the halogen elements, is referred to as suppressants, and can interfere with the kinetics of the catalytic reaction and deactivate it. This has made TCE and PCE difficult compounds to treat with a catalytic oxidizer unit.

Halogenated compounds have affected the long term durability of the catalyst materials, and inhibited short term performance. Recent innovations in the development and design of catalysts include formulations that are resistant to deactivation.

The recalcitrant nature of PCE has made it one of the most difficult materials to oxidize. Allied Signal has conducted extensive research in this area and has developed a new formulation of catalyst which, according to Allied Signal, oxidizes PCE in an efficient and cost effective manner.

TEST PROCEDURES

At the Savannah River Site (SRS) in South Carolina, the Westinghouse Savannah River Company (WSRC) is field-testing many technologies for use in remediating soil, groundwater and air contaminated with TCE and PCE. This testing is being done under the Integrated Demonstration Project. The best technologies will be used in future full- scale remediation systems at SRS.

One of the field tests was for Methanotrophic Bioremediation of TCE. This complex project tests a variety of new technologies, including horizontal wells, air sparging, vapor-phase injection of nutrients, and cometabolic bioremediation. Also tested was a catalytic oxidation treatment method for TCE and PCE-contaminated vapors produced from the vapor extraction system which were part of the methanotrophic bioremediation project.

The on site equipment consists of an air/methane injection system and a vapor extraction system. The vapor extraction system consists of a vacuum blower and an off-gas treatment system. The vacuum blower pulls 240 SCFM of air at -10 Inches Hg. from a horizontal well. This airstream contains PCE (approximately 150 ppm) and TCE (approximately 80 ppm). The vapor enters an oxidizer where it passes over the catalytic material. There is a Kilowatt Hour Meter dedicated to this oxidizer which monitors electrical use, and there is no primary heat recovery unit. This system is illustrated in Figure 1.

Gas samples were taken daily before the blower and at the exhaust stack. These samples were analyzed on site by a field laboratory. The equipment used for the analytical work consisted of a Hewlett-Packard Gas Chromatograph model 5890. The system has a packed column connected to a thermal conductivity meter for analysis of methane and CO_2, and a capillary column connected to a flame ionization detector for analysis of volatile organic compounds (TCE, PCE, vinyl chloride, dichloromethane, and dichloroethylene). All of the process equipment and the on site laboratory was designed, installed, and operated during the term of the project by ECOVA Corporation, an environmental services company located in Redmond, Washington.

To test the catalytic oxidation of TCE and PCE a new formulation of Allied Signal's HDC catalytic material was installed in the oxidizer on January 21, 1993. ECOVA operated the oxidizer with the new catalytic material from January 21 to April 30, 1993. The material consisted of four beds of catalyst, each one identical to the drawing in Figure 2.

RESULTS

Oxidation Efficiency

After installation, considerable attention was given to optimizing operating conditions. This primarily meant determining the minimum oxidizer temperature at which effluent concentrations of chlorinated hydrocarbons would meet discharge requirements.

Table 1 shows the results obtained during the three months of testing. Initially, poor reduction efficiency was obtained for PCE because temperatures were low. Over a period of a several days the oxidizer temperature was incrementally raised and samples taken to analyze conversion efficiency. This resulted in reduction efficiency for PCE of 95% or better for the duration of the test period. TCE was oxidized below detectable limits (5 ppm) at a temperature of 750°F. Table 2 shows the same data as Table 1, only sorted by catalyst temperature.

PCE required temperatures of 825°F. before effluent concentrations were below detectable limits. All daughter products of incomplete combustion were below detectable levels.

Energy Efficiency

Table 3 shows the electrical power usage per day for the oxidizer. Prior to January 21, 1993, the system was operated in a thermal mode. After the new catalytic material was installed, the oxidizer temperature was lowered from 1500°F. to approximately 825°F.

Electrical consumption per day during the thermal mode was approximately 2000 KWHR. While operating in the catalytic mode, electrical consumption per day was approximately 1000 KWHR.

Life Time Expectancy

The duration of this test was just slightly over three months. This is insufficient time to establish expected useful lifetimes.

Currently, Allied Signal is conducting laboratory tests on this material to confirm useful life. The warranted temperature of this material is 900°F., and long term tests are being performed that monitor destruction efficiency at approximately 1000°F.

CONCLUSIONS

This particular catalyst successfully achieved efficient oxidation of PCE. Because destruction of PCE has been difficult in the past, determining this ability was of primary importance.

Halogen suppression was not a problem. Suppression occurs when the halogens interfere with the kinetics of the catalytic oxidation reaction. If this were to occur, the suppression would be evident immediately. Since reduction efficiency was in excess of 95%, this past problem with catalysts does not appear to be a factor.

The catalyst has not been in use long enough to establish, with confidence, an expected useful life. Because other similar catalytic materials for treating TCE have demonstrated economically efficient life expectancies, determining this aspect of the new catalysts performance abilities was of less importance than reduction efficiency.

At $.03/KWHR, (the cost of electricity at SRS) use of this oxidizer cost approximately $30.00 per day.

This catalytic material appears to have useful applications in the remediation of sites contaminated with PCE. It achieves good reduction efficiency and does not seem to suffer from halogen suppression. Currently, it is being considered for use at SRS for full scale treatment systems.

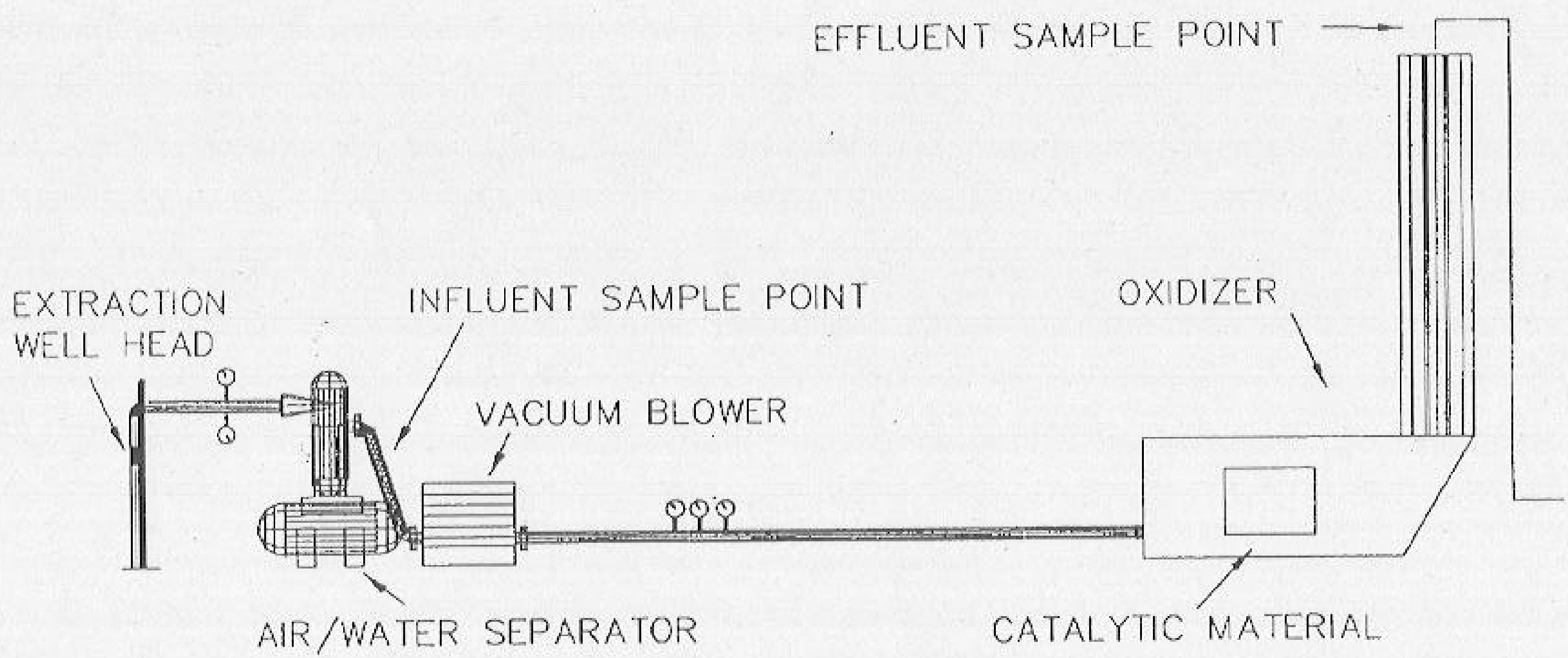
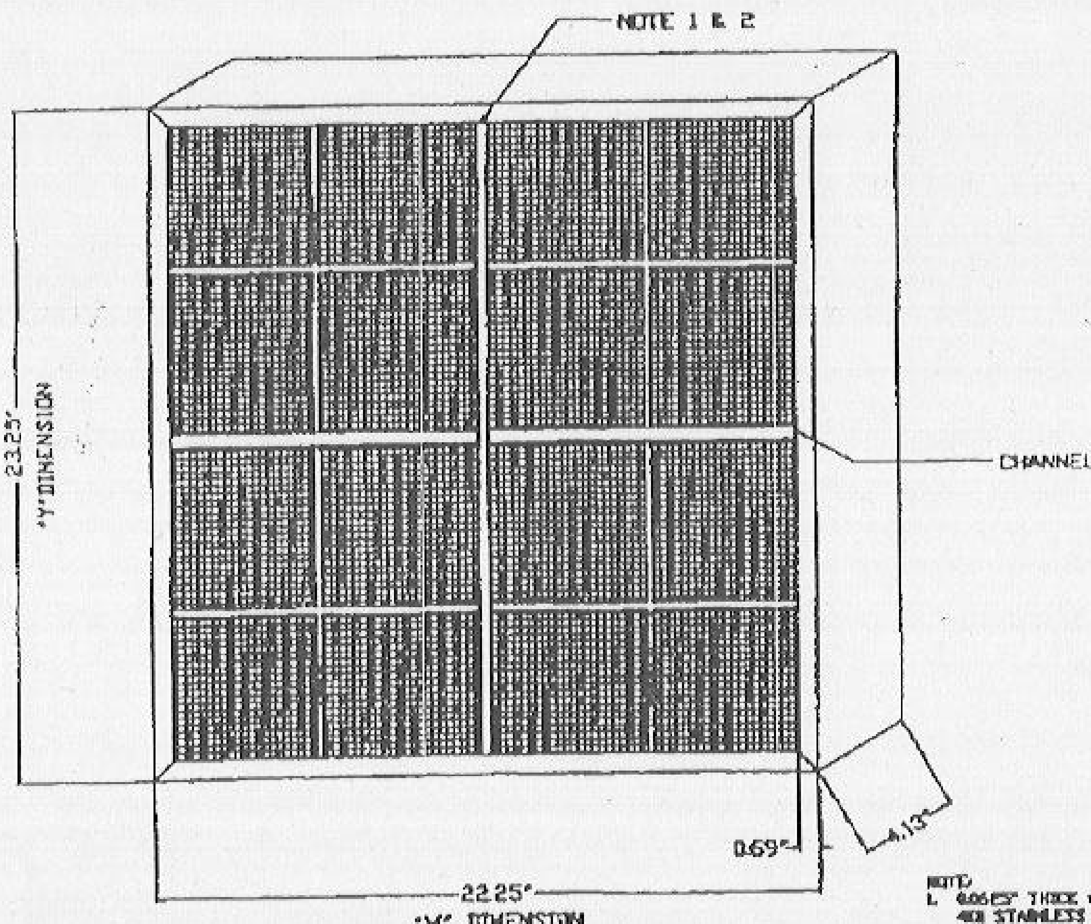

EFFLUENT SAMPLE POINT
EXTRACTION WELL HEAD
INFLUENT SAMPLE POINT
OXIDIZER
VACUUM BLOWER
AIR/WATER SEPARATOR
CATALYTIC MATERIAL

FIGURE 1

FIGURE 2



FRAMED ITEM - PART NO. 5550 IND-88

NOTE:
1. 0.0625" THICK x 3/4" WIDE 400 STAINLESS STEEL STRAP CENTERED OVER SAME GLUE JOINT FRONT AND BACK
2. BUTTWELD TO CHANNEL AND FRAME LIPS.
3. DIMENSIONAL TOLERANCE AFTER FRAMING ±1/32"
4. BLOCKS 16 PER 5.91" x 5.91" x 4.0" 400 CPSI

CATALYST FRAME
HDC-(PN) FULL FRAME
23.25" X 22.25" X 4.13"
50317-028-0

TESTDATA.XLS Chart 2

TABLE 1 - OPERATING EFFICIENCY

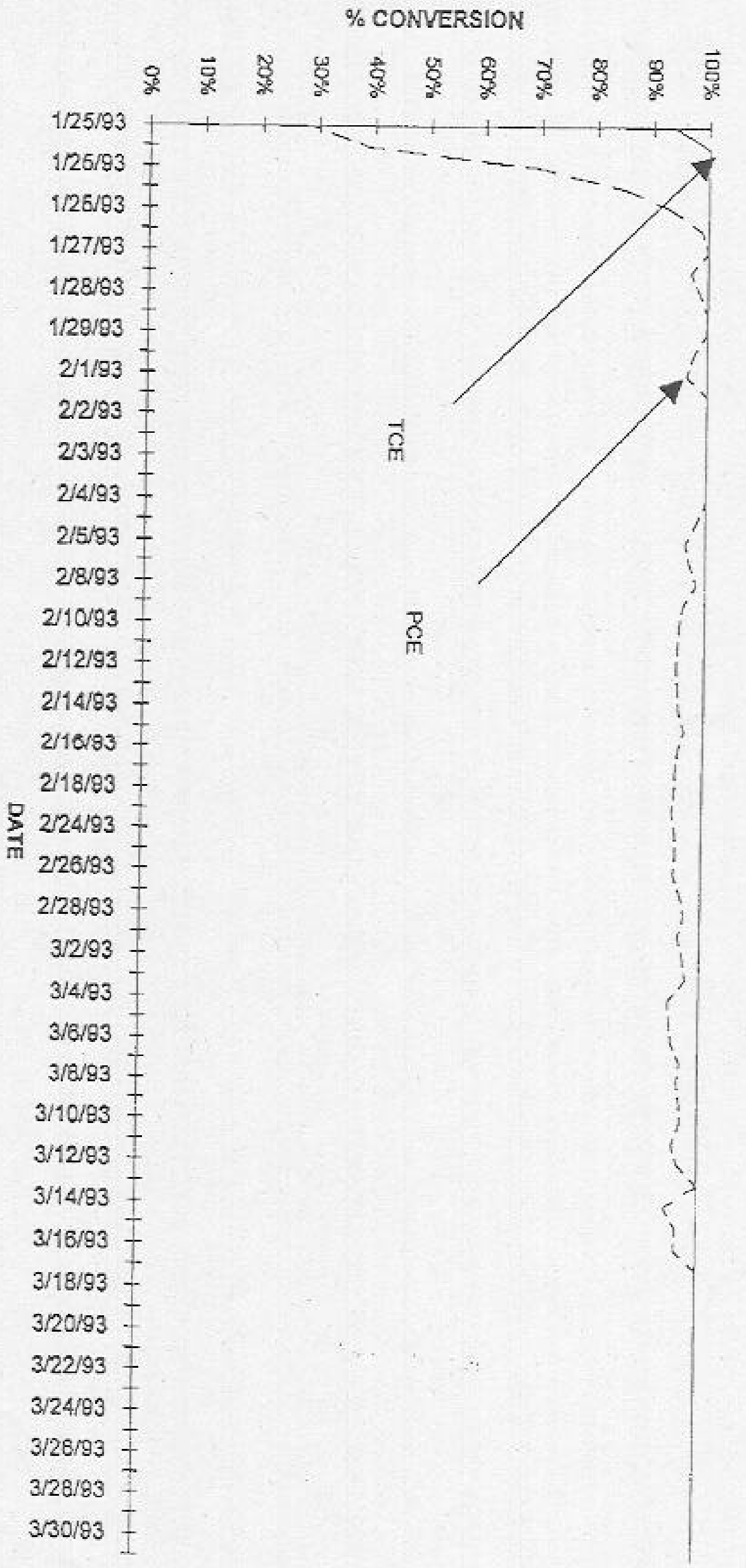
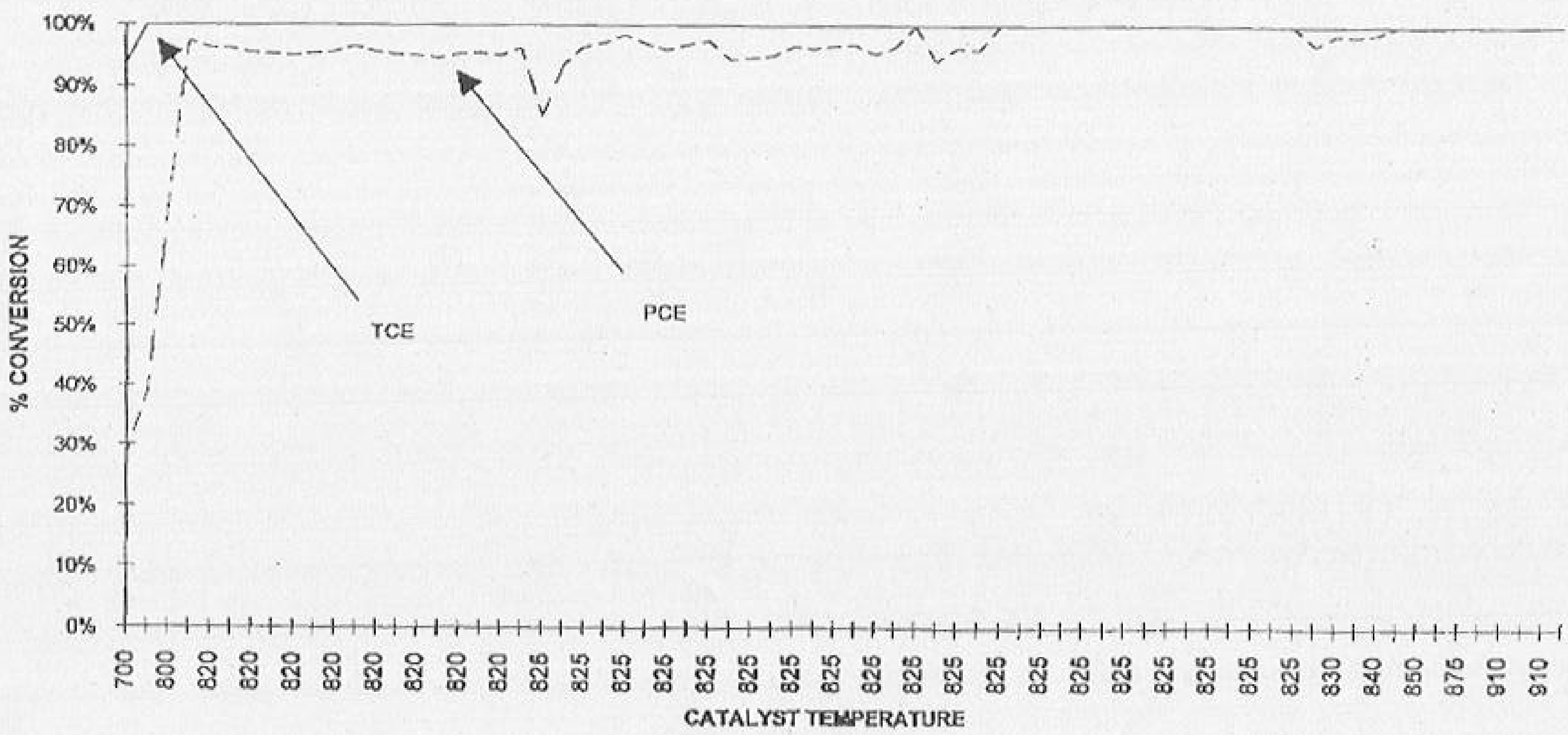


TABLE 2 - CONVERSION EFFICIENCY VS. TEMPERATURE



SUMMARY OF ALYTIC OXIDIZER PERFORMANCE

AICHE...r.XLS

CONCENTRATIONS LESS THAN 5 PPM ARE BELOW DETECTION LEVELS

DATE	SAMPLE #	INFLUENT TCE	INFLUENT PCE	INFLUENT VOC	EFFLUENT TCE	EFFLUENT PCE	EFFLUENT VOC	TEMP. DEG. F	% CONVERSION TCE	% CONVERSION PCE	% CONVERSION VOC
1/25/93		69.9	171.8	242.5	4.4	122.9	128.6	700	94%	28%	47%
1/25/93		69.9	171.8	242.5	0	105.3	107	750	100%	39%	56%
1/25/93		69.9	171.8	242.5	0	52	54.1	800	100%	70%	78%
1/25/93		69.9	171.8	242.5	0	25.52	31	825	100%	85%	87%
1/25/93		69.9	171.8	242.5	0	11.2	19.3	825	100%	93%	92%
1/26/93	3867	72	177.5	250	0	2.2	16	840	100%	99%	94%
1/27/93	3871	73	179	252	0	0	15	840	100%	100%	94%
1/27/93	3874	73	179	252	0	5.6	16.8	830	100%	97%	93%
1/28/93	3876	75	188	284	0	2.7	14	830	100%	99%	95%
1/28/93	3909	75	188	264	0	0.3	16.7	850	100%	100%	94%
1/29/93	3912	76.5	173.5	250	0	0.4	18	850	100%	100%	93%
1/31/93	3928	71	179	250	0	4.8	14	820	100%	97%	94%
2/1/93	3930	71	193	264	0	7	7	820	100%	96%	97%
2/2/93	3937	70	186	256	0	0	0	875	100%	100%	100%
2/2/93	3945	76	202	278	0	0	0	900	100%	100%	100%
2/3/93	3948	72	202	262	0	0	0	910	100%	100%	100%
2/3/93	3953	84	220	304	0	0	0	910	100%	100%	100%
2/4/93	3956	76.5	205.5	282	0	0	0	910	100%	100%	100%
2/4/93	3958	81	223	304	0	0	0	920	100%	100%	100%
2/5/93	3963	71	186	258	0	3.1	3.1	830	100%	98%	99%
2/5/93	3971	68	188	247	0	6.7	6.7	825	100%	96%	97%
2/7/93	3976	68	179	247	0	5	5	825	100%	97%	98%
2/8/93	3982	73	184.5	257.5	0	2.8	2.8	825	100%	98%	99%
2/9/83	3988	75	185	260	0	7	7	820	100%	96%	97%
2/10/93	3995	74	201	275	0	9	9	820	100%	96%	97%
2/11/93	3998	46	129.5	175.5	0	6	6	820	100%	95%	97%
2/12/93	4032	72	195	267	0	9.6	9.6	820	100%	95%	96%
2/13/93	4053	71	196	267	0	9	9	820	100%	95%	97%
2/14/93	4057	76	206	282	0	9	9	820	100%	96%	97%
2/15/93	4062	75	208	284	0	7	7	820	100%	97%	98%
2/16/93	4069	75	207	281	0	9	9	820	100%	96%	97%
2/17/93	4075	76	210	286	0	10	10	820	100%	95%	97%
2/18/93	4082	80	226	306	0	11	11	820	100%	95%	96%
2/19/93	4090	78	208	288	0	11	11	820	100%	95%	96%

2/24/93		4098	78	215	293	0	10	10	820	100%	95%	97%
2/25/93		4101	79	221	300	0	10	10	820	100%	95%	97%
2/26/93		4140	75	205	281	0	10	10	820	100%	96%	96%
2/27/93		4147	74	193	267	0	7	7	820	100%	96%	97%
2/28/93		4149	75	208	283	0	6	6	825	100%	97%	98%
3/1/93		4159	73	204	277	0	8	8	825	100%	96%	97%
3/2/93		4162	72	199	271	0	6	6	825	100%	97%	98%
3/3/93		4190	73	206	279	0	5	5	825	100%	98%	98%
3/4/93		4201	73	199	273	0	11	11	825	100%	94%	96%
3/5/93		4238	76	211	287	0	11	11	825	100%	95%	96%
3/6/93		4269	71	185	256	0	9	9	825	100%	95%	96%
3/7/93		4276	78	215	283	0	7	7	825	100%	97%	98%
3/8/93		4282	77	216	293	0	8	8	825	100%	96%	97%
3/9/93		4285	78	217	295	0	7	7	825	100%	97%	98%
3/10/93		4294	69	193	262	0	6	6	825	100%	97%	98%
3/11/93		4301	70	198	268	0	9	9	825	100%	95%	97%
3/12/93		4337	74	205	279	0	7	7	825	100%	97%	97%
3/13/93		4359	69	200	269	0	0	0	825	100%	100%	100%
3/14/93		4361	70	174	244	0	10	10	825	100%	94%	96%
3/15/93		4367	72	194	266	0	7	7	825	100%	96%	97%
3/16/93		4371	74	203	278	0	8	8	825	100%	96%	97%
3/17/93		4378	67	179	246	0	0	0	825	100%	100%	100%
3/18/93		4389	72	192	265	0	0	0	825	100%	100%	100%
3/19/93		4428	69	177	246	0	0	0	825	100%	100%	100%
3/20/93		4448	83	175	239	0	0	0	825	100%	100%	100%
3/21/93		4451	58	155	213	0	0	0	825	100%	100%	100%
3/22/93		4457	59	163	223	0	0	0	825	100%	100%	100%
3/23/93		4464	62	173	235	0	0	0	825	100%	100%	100%
3/24/93		4472	59	172	231	0	0	0	825	100%	100%	100%
3/25/93		4487	67	184	251	0	0	0	825	100%	100%	100%
3/26/93		4529	53	164	217	0	0	0	825	100%	100%	100%
3/27/93		4551	62	170	232	0	0	0	825	100%	100%	100%
3/28/93		4567	63	189	252	0	0	0	825	100%	100%	100%
3/29/93		4577	60	156	217	0	0	0	825	100%	100%	100%
3/30/93		4584	73	204	277	0	0	0	825	100%	100%	100%
3/31/93		4619	68	191	259	0	0	0	825	100%	100%	100%
4/1/93		4628	71	181	252	0	0	0	825	100%	100%	100%
4/2/93		4667	71	182	253	0	0	0	825	100%	100%	100%
4/3/93		4683	75	199	274	0	0	0	825	100%	100%	100%
4/4/93		4689	76	209	285	0	6	6	825	100%	97%	98%
4/5/93		4694	68	177	243	0	0	0	825	100%	100%	100%
4/6/93		4706	70	198	266	0	6	6	825	100%	97%	98%
4/7/93		4709	70	191	261	0	0	0	825	100%	100%	100%
4/8/93		4717	70	192	262	0	0	0	825	100%	100%	100%
4/9/93		4758	66	176	242	0	0	0	825	100%	100%	100%
4/10/93		4764	71	196	267	0	0	0	825	100%	100%	100%

4/11/93		4766	68	170	238	0	0	0	825	100%	100%	100%
4/12/93		4777	68	195	262	0	0	0	825	100%	100%	100%
4/13/93		4781	67	187	254	0	0	0	825	100%	100%	100%
4/14/93		4788	69	187	256	0	0	0	825	100%	100%	100%
4/15/93		4816	68	179	247	0	0	0	825	100%	100%	100%
4/16/93		4854	72	173	246	0	6	6	825	100%	97%	98%
4/17/93		4886	68	187	255	0	0	0	825	100%	100%	100%
4/18/93		4889	68	187	255	0	0	0	825	100%	100%	100%
4/19/93		4894	63	168	232	0	0	0	825	100%	100%	100%
4/20/93		4906	70	198	269	0	0	0	825	100%	100%	100%
4/21/93		4910	67	187	254	0	0	0	825	100%	100%	100%
4/22/93		4918	73	202	275	0	0	0	825	100%	100%	100%
4/24/93		4938	43	110	153	0	0	0	825	100%	100%	100%
25/93 7:38		4943	58	168	226	0	0	0	825	100%	100%	100%
4/26/93		4850	48	119	168	0	0	0	825	100%	100%	100%
4/27/93		4958	69	223	291	0	0	0	825	100%	100%	100%
4/28/93		4968	67	232	300	0	4	4	825	100%	98%	99%
4/29/93		4975	64	187	251	0	6	6	825	100%	97%	98%
4/30/93		5037	52	142	194	0	6	6	825	100%	96%	97%

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